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Polyfunctional Heterogeneous Catalysis

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I. Introduction

Reaction mechanisms which involve successive reaction steps, and therefore chemical intermediates, have been discussed in many areas of chemical experience. They are notably familiar in biochemistry, where metabolic and synthesis reactions occur as a result of chains of successive reaction steps. Often, individual steps are catalyzed by various and different enzymes. Similarly, the concept of catalysis of successive reaction steps by different catalytic centers or materials has been suggested early in the history of man-made catalysis—for example, in the case of the Fischer-

Tropsch catalyst (see, e.g., ref. 1). On various occasions such cooperative action has been hypothesized (see, e.g., the review by Natta and Rigamonti, 2) to explain the performance of solid catalytic materials prepared from more than one chemical ingredient, and presumed not to constitute a single, homogeneous chemical composition ("Mehrstoffkatalysator"). The existence of such action, cooperative through the mediation of reaction intermediates, has been largely speculative. Its direct and specific demonstration has been difficult, since other modes of coaction by different chemical components of a catalytic mass can occur, such as, for example, electronic modification of a solid composition by an "impurity"; or, catalysis by the *boundary* structure existing *between* two distinct chemical phases.

During recent years, studies of a number of hydrocarbon transformations catalyzed by porous solid oxides containing a transition metal, notably platinum, have evolved some concrete examples and demonstrations of truly polystep catalytic reactions. Specifically, these reactions have been shown to be performed by catalysts which contain geometrically separate and different catalyst components, each of which catalyzes separate steps. The chemical intermediates exist as true compounds, although often at undetected concentrations. The term "true" is used in this context to characterize the intermediate as a normal chemical species, existing independently of, and desorbed from, the catalyst phase, and subject to ordinary physical laws of diffusion.

From such hydrocarbon reaction studies emerges an understanding of some of the characteristics of such polystep catalytic reactions, and of some of the basic physical requirements which must be fulfilled in order for the purely formal kinetic scheme of successive reactions to be operative in physical reality.

II. Principles of Polystep Catalysis

A. SINGLE OR MULTIFUNCTIONAL CATALYSTS

If a catalyst mass contains only one type of catalytic site we shall call it a *monofunctional* catalyst. By one "type" is meant that every catalytic site or surface exhibits the same *qualitative* catalytic property as to what reaction or reaction steps it can catalyze. We shall concern ourselves only, of course, with reaction steps which are thought to be relevant to the reaction examined. For example, we normally assume that platinum/charcoal is a monofunctional catalyst in the hydrogenation of olefins. (For the present purpose we need not be concerned about the *quantitative* equivalence of every Pt-surface site, i.e., whether or not there is uniformity or a spectrum of catalytic effectiveness for the same reaction among different platinum sites.)

The term "monofunctional" refers to the intrinsic activity of a catalyst in contact with a second material. The activity of a metal may differ depending on the nature of the reaction. This may be due to varying degrees of surface effects of electronic interrelationships of the metal. In such cases, the activity depends on the nature of the surface constituent, and we still have a monofunctional catalyst.

In contrast, we shall see that a multifunctional catalyst, such as the silica-alumina catalyst, has more than one reaction step than do the monofunctional catalysts. The reactions of the other components are relevant to accomplish the overall reaction system.

In a polyfunctional catalytic reaction, the catalyst is responsible for distinctly different "components."

B. INTERMEDIATE

1. Definition

It is important to recognize the term "intermediate" in this context. The use of the term "surface complex," or "activated complex," in heterogeneous catalysis, the combined or, by specific force-field interactions, a molecule. In contrast to this, the term "intermediate" refers to a chemical species that is a normal chemical species, i.e., with thermodynamic properties not unlike those of compounds.

2. Physical Meaning of Reaction

The concept of reaction in the picture of reaction kinetics is

where A , B , C are gas phase (or liquid phase) species. In the example discussed is the sequence of reactions counteracted in the dehydrogenation of

occasions such cooperative by Natta and Rigamonti, materials prepared from not to constitute a single, katalysator"). The existence of reaction intermediates and specific demonstration on by different chemical species, for example, electronic activity"; or, catalysis by the chemical phases.

hydrocarbon transformations transition metal, notably platinum and demonstrations of these reactions have been in geometrically separate sites catalyzes separate steps. compounds, although often attributed in this context to characteristic species, existing independently, and subject to ordinary

enlarges an understanding of catalytic reactions, and of some to be fulfilled in order for the reactions to be operative in

Catalysis

CATALYSTS

A catalytic site we shall call it meant that every catalytic property as to what all concern ourselves only, to be relevant to the reaction that platinum/charcoal catalyzes the hydrogenation of olefins. (For the sake of the quantitative equivalent there is uniformity or a reaction among different

The term "monofunctional" does not exclude the possibility that the intrinsic activity of a catalytic material may be influenced by chemical contact with a second material. Thus the intrinsic hydrogenation activity of a metal may differ depending on the nature of the support. Such effects may be due to varying degrees of metal dispersion, or due to more profound effects of electronic interaction which modify the electronic properties of the metal. In such cases, although the activity of the metal may depend on the nature of the support, the *locus* of activity is still at the metal constituent, and we still have a case of monofunctionality.

In contrast, we shall see that in a paraffin isomerization system a platinum on silica-alumina catalyst is a *multifunctional*, specifically, a *bifunctional* catalyst; the platinum sites catalyze distinctly different reactions and reaction steps than do the silica-alumina sites; neither catalyze the reactions of the other component; furthermore, both types of reactions are relevant to accomplish the over-all reactions of the desired conversion system.

In a polyfunctional catalytic solid, we shall refer to the materials or sites responsible for distinctly different reactions or reaction steps as catalyst "components."

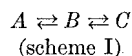
B. INTERMEDIATES AND REACTION SEQUENCES

1. Definition

It is important to recognize the specific meaning of the term "intermediate" in this context. The use of the term will *not* relate to the concept of "surface complex," or "activated complex"; for, in this case, at least in heterogeneous catalysis, the catalyst, or a part of it, is structurally combined or, by specific force-fields, is interacting with a reaction-participating molecule. In contrast to this meaning, the term "intermediate" here will refer to a chemical species that is produced by the catalyst as a desorbed, normal chemical species, i.e., one that has its own name, structure, and thermodynamic properties normally associated with independent chemical compounds.

2. Physical Meaning of Reaction Sequences

The concept of reaction intermediates is linked intimately with any picture of reaction kinetics that includes successive reactions, such as

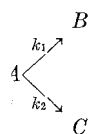


where *A*, *B*, *C* are gas phase (or liquid phase), i.e., *desorbed* species. A much discussed example is the sequence cyclohexane-cyclohexene-benzene encountered in the dehydrogenation catalysis by chromia-alumina (3).

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when the rate-constants of
he rate-constants of inter-

II can behave in a manner



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 B and C .

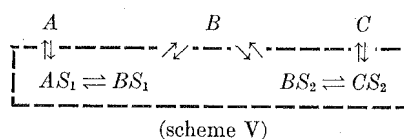
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thoroughly the problem of
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realize that scheme I as well
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n the form of a gas phase
of the applicability of this

formal analogue. An examination of the detailed physical situation, scheme II, however, places some important limitations on the nature of B as a truly necessary "intermediate": a molecule once adsorbed and reacted to the form BS may desorb but may also react further to CS . The magnitudes of the various rate constants express the relative probability for these events. Molecules of C can arise which never existed in the gas phase as B . The species B is not by necessity a gas phase intermediate. In fact, there is no concrete significance to B being an "intermediate" as long as the entities BS which transform to C are chemically indistinguishable as to whether they were created from AS by surface reaction, or from readsorption on S of a gas phase molecule B . This situation exists in the case of a monofunctional catalyst system, where only *one type* of catalytic site S exists which can form only one type of BS complex.

On the other hand, where the conversion steps A to B and B to C are catalyzed by two qualitatively different and distinct catalytic sites S_1 and S_2 , scheme II becomes



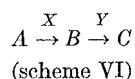
and thus B attains unqualified significance as a true intermediate in a *bifunctional catalyst system*.

3. The Potential Role of Quasi-Intermediates of Monofunctional Reaction Sequences

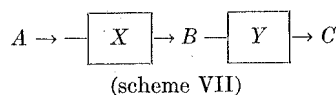
There remains an important potential role, however, for the gas phase product B in a monofunctional reaction sequence: we can profoundly affect the rate of conversion to the monofunctional reaction product C by "operating on" the gas phase B molecules. If we remove B from the gas phase at a fast enough rate we can decrease the steady-state concentration of B , and thus of the species BS which generates C . Thus, although the *concentration* of B in the usual reaction $A \rightarrow C$ may be so small as to remain unnoticed or undetectable, the provision of a large enough *rate* for its removal can effectively divert the previous path of the monofunctional reaction. Such rate of removal of B may be provided by the presence of another catalyst material which removes B by conversion to a new species. Thus, we shall call the product B of the monofunctional reaction a "quasi-intermediate" because it has the potential of becoming a true intermediate in a polyfunctional catalysis system. This phenomenon is an important one connected with catalyst *selectivity*, as will be discussed later.

C. TRIVIAL AND NONTRIVIAL POLYSTEP REACTION

We shall now examine specifically the nature of the *polyfunction* reaction sequence involving a true intermediate, where the analogue of scheme I is applicable. If a chemical transformation $A \rightarrow B$ is known to be accomplished in the presence of catalytic material X , and the conversion $B \rightarrow C$ is known to proceed on catalyst Y , then the reaction

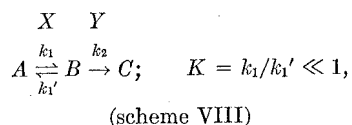


can obviously be accomplished in successive reaction zones:



If high conversion can be achieved for each step under similar catalytic conditions, the two reaction zones may be combined and a basically similar over-all conversion would be expected. Such a case of a polystep chemical reaction can be considered trivial.

On the other hand, if the first reaction step is greatly limited in attainable conversion for reasons of thermodynamic equilibrium, i.e.,



then a consecutive operation of scheme VII above cannot lead to anything more than negligible over-all conversion. Nevertheless, the formal mathematical treatment of the kinetic scheme (VIII) permits any desired net reaction rate and therefore any desired conversion. For example, treating all steps as first-order steps, the maximum concentration of B is

$$[B] = [A] \frac{1}{(1/K) + (k_2/k_1)} \quad (1)$$

and can be arbitrarily small. On the other hand, the rate of the over-all reaction is

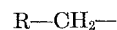
$$\frac{dN}{dt} = [A]k''; \quad k'' = k_2 \frac{1}{(1/K) + (k_2/k_1)} \quad (2)$$

and the value of k'' can be made arbitrarily large by appropriate choice of the rate constants k_1 and k_2 . The magnitude of the attainable conversion

ϵ_{AC} can then be greater than attainable in separate success

This will serve as a *definition*

As an example, a hydrocarbon manner that the first reaction olefin. Such a reaction is characterized by a constant for the dehydrogenation



which is shown by the data in

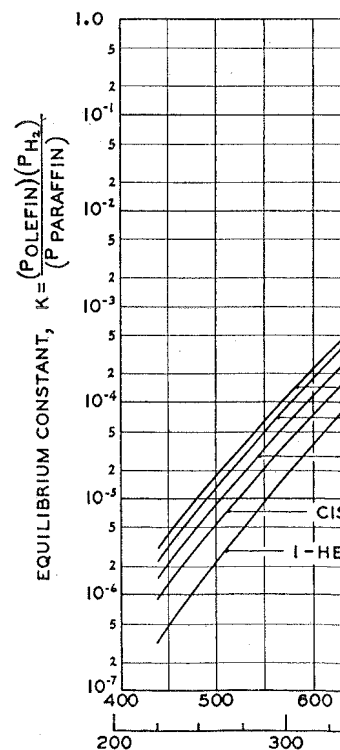


FIG. 1. Equilibrium constants and drogenation of *n*-hexane to hexenes

EP REACTION

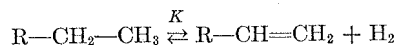
the *polyfunction* reaction
 analogue of scheme I is
 is known to be accom-
 and the conversion $B \rightarrow C$
 ion

ϵ_{AC} can then be greater than the product of the conversions individually attainable in separate successive steps,

$$\epsilon_{AC} \gg \epsilon_{AB} \times \epsilon_{BC} \quad (3)$$

This will serve as a *definition of the nontrivial polystep reaction*.

As an example, a hydrocarbon reaction might be carried out in such a manner that the first reaction step be a dehydrogenation to the respective olefin. Such a reaction is characterized by a thermodynamic equilibrium constant for the dehydrogenation step,



which is shown by the data in Fig. 1 for the hexane-hexene equilibrium.

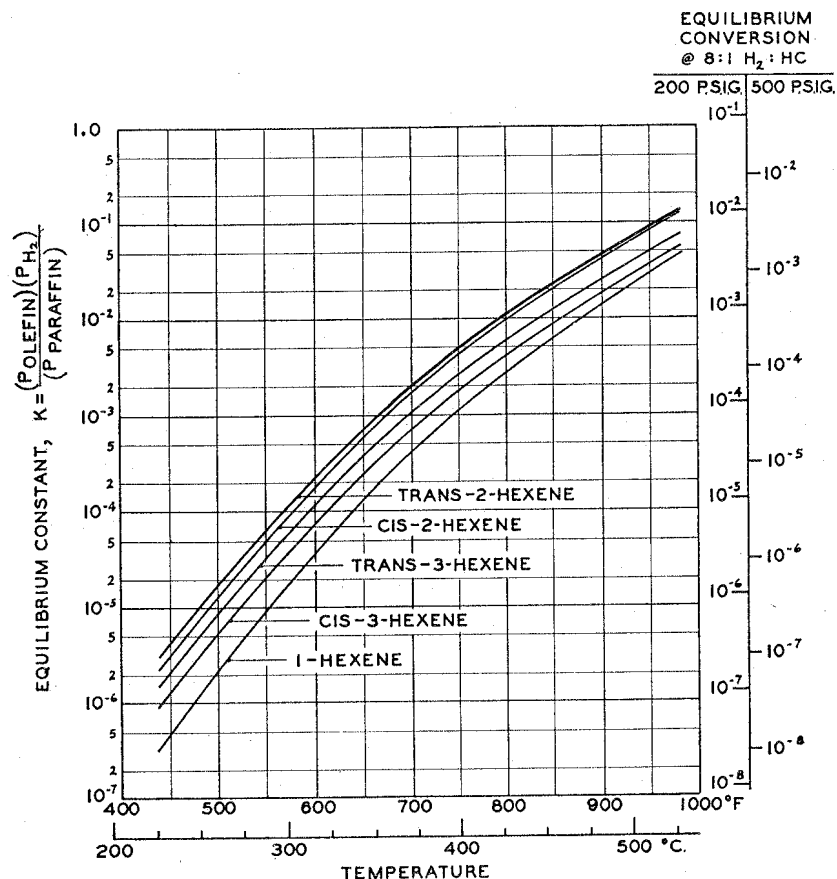


FIG. 1. Equilibrium constants and some typical equilibrium conversions for the dehydrogenation of *n*-hexane to hexenes.

The maximum attainable conversion of paraffin to a corresponding olefin is obtained from

$$\frac{[\text{olefin}]}{[\text{paraffin}]} = \frac{K}{[\text{H}_2]_{(\text{atm.})}}$$

At 435°C the olefin concentration is found to be only about 0.02% at 30 atm. partial pressure of hydrogen. Thus, if we were to carry out paraffin isomerization by successive and separate steps of dehydrogenation of *n*-paraffin to *n*-olefin, followed separately by skeletal isomerization of the *n*-olefin produced to iso-olefin (and subsequent rehydrogenation), the over-all conversion of such a scheme could be, at best, 0.02%. Thus, the paraffin isomerization, if accomplished in a bifunctional reaction system with a high conversion as might be described by formula (2), is an example of a nontrivial case as defined by (3) above.

D. MASS-TRANSPORT IN POLYSTEP REACTION

Why is it that the operation (VII) does not accomplish the high rate of conversion which the formal derivation of (1) and (2) allows for the scheme VI? The over-all reaction rate is limited by the rate of transport of intermediate product *B* from the generation zone to the sites for re-reaction, and this process is not taken into account in deriving (2). In the case of successive reaction zones, with a reactant flow rate *F*, the rate of transport of intermediate will be $F\epsilon_{AB}$, and over-all conversion, therefore, will be limited to this rate.

The necessity of molecular transport must obviously arise whenever the reaction sites *X* and *Y* are not in geometrically identical locations, and it is precisely this condition that characterizes an important requirement for the multifunctional catalyst. In the case of a catalyst solid that consists of a composite of *X*-sites and *Y*-sites in a single reactor zone the physical transport of intermediates between *X*- and *Y*-sites must proceed by a diffusion process, which then becomes an important and integral link in the chain of reaction events.

1. The Simplest Model of Separate Catalytic Surfaces

Let catalytic *X*-sites exist on a plane, and catalytic *Y*-sites on another plane located parallel to the first, at a distance $x = L$ in space. For the consecutively catalyzed reaction scheme VIII, intermediate *B* molecules must now diffuse from $x = 0$ to $x = L$ through a medium having diffusivity *D*.

We shall then have (in the steady state; all steps taken as first-order; dN/dt = over-all rate per unit surface area):

For the first reaction step

$$\frac{dN}{dt} =$$

For the second reaction

From the law of diffusion

$$\frac{d}{dt}$$

From these equations we obtain actual rate as

$$\frac{dN}{dt} = [A]k'' \left(1 + \right)$$

to be compared with formula (2). Thus the effectiveness factor

It follows from $k'' \rightarrow \infty$ that the rate, regardless of how high

$$\left(\frac{dN}{dt} \right)$$

2. Model of Multifunctional Catalyst

In the case of the multifunctional hydrocarbon reactions, the model above. In the model, the volume of space where catalysis occurs only at its boundaries. In a solid space is permeated by catalytic sources or sinks.

For this case a convenient model of a multifunctional catalyst solid consists of a composite of two types of particles, one component containing only one type of site, the other containing both types. This structure has been experimentally realized. The larger granules are composed of the two types of sites.

$$\frac{dN}{dt} = k_1[A] - k_1'[B]_{x=0}; \quad K = \frac{k_1}{k_1'} \quad (4)$$

For the second reaction step

$$\frac{dN}{dt} = k_2[B]_{x=L}$$

From the law of diffusion

$$\frac{dN}{dt} = \frac{D}{L} ([B]_{x=0} - [B]_{x=L})$$

From these equations we can eliminate $[B]_{x=0}$ and $[B]_{x=L}$, and obtain the actual rate as

$$\frac{dN}{dt} = [A]k'' \left(1 + \frac{k'' L}{K D}\right)^{-1}; \quad k'' = k_2 \frac{1}{(1/K) + (k_2/k_1)} \quad (5)$$

to be compared with formula (2) for the case of purely chemical kinetics. Thus the effectiveness factor η is

$$\eta = \frac{1}{1 + \frac{k'' L}{K D}} \quad (6)$$

It follows from $k'' \rightarrow \infty$ that there is an absolute ceiling to attainable rate, regardless of how high the effective catalytic rate constant might be, of

$$\left(\frac{dN_s}{dt}\right)_{\max} = [A]K \frac{D}{L} = [B_{\text{eq}}] \frac{D}{L} \quad (7)$$

2. Model of Multifunctional Porous Solid Catalyst Systems

In the case of the multifunctional porous catalysts, such as are familiar in hydrocarbon reactions, the situation is somewhat different from that in the model above. In the model above, the diffusion problem is confined to a volume of space where catalytic activities (the sources and sinks) occur only at its boundaries. In the present case a volume element of (porous solid) space is permeated by both diffusive resistance *as well as* distributed catalytic sources or sinks.

For this case a convenient model for analysis is pictured in Fig. 2. The catalyst solid consists of a mixture of two distinct types of component particles, one component containing catalytic sites of type X only in its pore structure, the other containing sites of type Y only. This model is one that has been experimentally realized (see Sections III-V). A mechanical mixture is made of the two catalyst components in powder form, from which the larger granules are composited by pressing or extruding. In such a

model we can consider the gas spaces between the component particles as "short circuits," i.e., offering no diffusional resistance compared to the intraparticle diffusional problem *within* each *component* particle: Effective diffusivities in free gas space are one to two orders of magnitude larger than those within high-surface-area solids, and the average *interparticle*

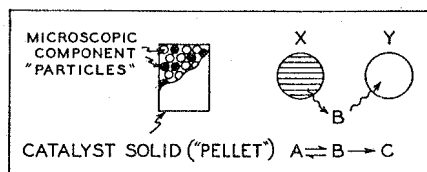


FIG. 2. Model of a two-component catalytic solid, consisting of separate particles of catalyst compounds *X* and *Y*.

distances are smaller than the particle diameters by nearly an order of magnitude (e.g., compare the dimensions of the voids between packed spheres with the diameters of the spherical particles). The problem of mass transport of the intermediate molecules between *X* and *Y* catalyst sites can thus be formulated as an *intraparticle* diffusion problem, involving separately the particles *X* and those of *Y* by conventional analysis.

For each of the *X*- and *Y*-particle systems the concentration of the intermediate species *B* has to satisfy a diffusion equation

$$D\nabla^2[B] \pm \frac{dB}{dt} = 0 \quad (8)$$

with *B*-generation (+), and *B*-consumption (−) within the *X*- and *Y*-systems, respectively; in addition, we have two conditions connecting the systems.

(1) The steady state rates of generation of *B* in the *X*-system and consumption in the *Y*-system are equal, and are identical with the over-all reaction rate

$$\frac{dN}{dt} = \left(\frac{dB}{dt}\right)_X = -\left(\frac{dB}{dt}\right)_Y \quad (9)$$

(2) There is a common boundary condition for the *X*- and *Y*-systems:

$$\text{at } r_X = R_X, \text{ and } r_Y = R_Y: [B]_X = [B]_Y = B_0, \quad (10)$$

i.e., the concentration at the particle boundaries is equal and is the concentration in *inter*-particle space.

Let us now examine the polystep reaction of scheme VIII.* We shall assume the kinetics of all steps to be first-order in the respective reactants.

* Component particle sizes and diffusivities will be taken as equal for both component systems.

For the *Y*-system we are dealing with the utilization factor η (which uninhibited reaction rate is attained)

$$\eta_Y = \frac{3}{\varphi_Y}$$

where

For the *X*-system, we must take into account the reaction rates,

$$\frac{dB}{dt}$$

With

K

and B_{eq} being the equilibrium concentration of *B*,

$$\frac{dB}{dt} =$$

This rate, when substituted into eq. (9) in functional form as (12Y) with

φ_X

The functional form of η in terms of measured parameters, and (9),

$$\frac{dN}{dt}$$

and for the *X*-system, from (13X)

$$\frac{dN}{dt} [B]$$

the component particles as resistance compared to the *component* particle: Effective orders of magnitude larger and the average *interparticle*

For the *Y*-system we are dealing with the basic case of the rate of consumption of the reactant *B* that is the intermediate in the over-all reaction,

$$-\frac{dB}{dt} = k_2[B] \quad (11Y)$$

which, placed into (8), results in the well known form (references 6-8) for the utilization factor η (which indicates what *fraction* of the diffusion-uninhibited reaction rate is attained).

$$\eta_Y = \frac{3}{\varphi_Y} \left(\frac{1}{\tanh \varphi_Y} - \frac{1}{\varphi_Y} \right) \quad (12Y)$$

where

$$\varphi_Y = R \sqrt{\frac{k_2}{D}} \quad (13Y)$$

For the *X*-system, we must take into account the forward and backward reaction rates,

$$\frac{dB}{dt} = k_1A - k_1'B$$

With

$$K = \frac{k_1}{k_1'} = \frac{B_{eq}}{A}$$

and B_{eq} being the equilibrium concentration of *B* in $A \rightleftharpoons B$, we can write

$$\frac{dB}{dt} = \frac{k_1}{K} ([B_{eq}] - [B]) \quad (11X)$$

This rate, when substituted into (8), results in a solution for η_X of the same functional form as (12Y) with

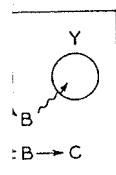
$$\varphi_X = R \sqrt{\frac{k_1}{KD}} \quad (13X)$$

The functional form of η in each case is such that negligible diffusion effects will result when $\varphi < 1$. This condition can also be expressed in terms of measured parameters: For the *Y*-system, from (13Y), (11Y), and (9),

$$\frac{dN}{dt} \frac{1}{[B]} \frac{R^2}{D} < 1 \quad (14Y)$$

and for the *X*-system, from (13X) (11X), and (9),

$$\frac{dN}{dt} \frac{1}{[B_{eq}] - [B]} \frac{R^2}{D} < 1$$



consisting of separate particles of

eters by nearly an order of the voids between packed (particles). The problem of mass between *X* and *Y* catalyst sites diffusion problem, involving conventional analysis.

he concentration of the inter- quation

0 (8)

(-) within the *X*- and *Y*- two conditions connecting the

B in the *X*-system and con- ce identical with the over-all

$$\left(\frac{dB}{dt} \right)_Y \quad (9)$$

m for the *X*- and *Y*-systems:

$$x = [B]_Y = B_0, \quad (10)$$

aries is equal and is the con-

m of scheme VIII.* We shall er in the respective reactants.

be taken as equal for both compo-

3. A General Criterion for Polystep Reaction Systems

Regarding the over-all reaction effect, the kinetics (1) and (2) lead to $[B]$ approaching $[B_{eq}]$ if the first reaction step is already adequately fast, so that (14Y) of the *Y-system* will be the limiting condition, with $B \rightarrow B_{eq}$. On the other hand, the kinetics (1) and (2) leads to $[B] \ll [B_{eq}]$ when the first reaction step is limiting, and thus when (14X) is controlling, we have $B_{eq} - B \rightarrow B_{eq}$. It follows, in view of (10), that the expression

$$\frac{dN}{dt} \frac{1}{[B_{eq}]} \frac{R^2}{D} < 1 \quad (15)$$

applies generally to the system as a whole.

The relative insensitivity of this type of diffusion criterion to particle shape and to assumption of exact kinetics, has been discussed in connection with the macroscopic reactant diffusion problem on catalyst granules (7). The condition (15) is a general order-of-magnitude criterion defining the physical conditions of intimacy between the component systems for no mass-transport inhibition. It defines a requirement for realizing the formal kinetics of polystep reactions.

We can rewrite (15) in terms of a partial pressure requirement for the intermediate species, since

$$[B_{eq}] = 4.4 \times 10^{-5} \left(\frac{273}{T} \right) \times P_{B,eq}$$

where

$$[B_{eq}] = [\text{moles/cm.}^3], \quad T = [^\circ\text{K.}], \quad P_B = [\text{atm.}]$$

We obtain

$$P_B > 2.3 \times 10^4 \left(\frac{T}{273} \right) \frac{dN}{dt} \frac{R^2}{D} \quad (15a)$$

Figure 3 shows typical requirements for the maximum size of catalyst component particles for a typical magnitude (δ) of diffusivity ($D = 2 \times 10^{-3}$ cm.²/sec.), and reaction rate ($dN/dt = 10^{-6}$ moles/sec. cm.³), as a function of the equilibrium concentration (expressed as partial pressure) which the chemical intermediate can attain.

It is interesting to note that a degree of intimacy of a magnitude which is still realizable by mechanical mixing, such as $R = 10^{-4}$ cm. = 1μ can still support a reaction if a gas phase intermediate can be produced with a partial pressure as low as 10^{-7} atm.

Such considerations serve to demonstrate that polystep reactions may easily

proceed with intermediates at detection.

Aside from defining the size of catalyst composite, R also de-

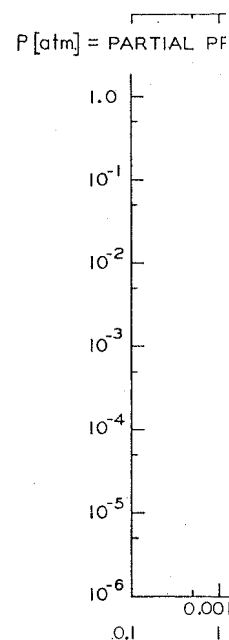


FIG. 3. Intimacy requirement, conditions of reaction rate (10^{-6} moles of intermediate).

degree of heterogeneity in regions or patches of catalyst

E. SELECTIVITY I

We have noted in Section while generating a desired product termed "quasi-intermediate component Y may then lead to diverting old product C into

proceed with intermediates at concentrations far below the limit of experimental detection.

Aside from defining the size of distinct component particles in a mixed catalyst composite, R also defines a maximum allowable magnitude for the

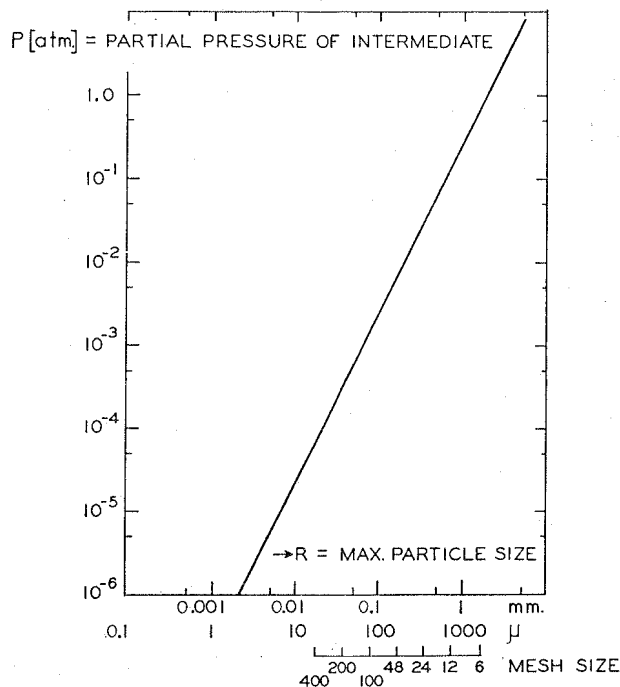
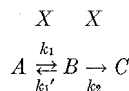


FIG. 3. Intimacy requirement, in terms of component particle size, for typical conditions of reaction rate (10^{-6} moles/sec cm^3), as a function of equilibrium vapor pressure of intermediate.

degree of heterogeneity in a catalyst mass as regards the distribution of regions or patches of catalytic activity of the two types.

E. SELECTIVITY IN THE POLYFUNCTIONAL CATALYST

We have noted in Section II,B,3 that a single monofunctional catalyst while generating a desired product may give rise to species which we have termed "quasi-intermediates." The introduction of a different catalyst component Y may then lead to *interception* of the usual reaction path, diverting old product C into a new product D :



items

inetics (1) and (2) lead to is already adequately fast, g condition, with $B \rightarrow B_{eq}$. ds to $[B] \ll [B_{eq}]$ when the $4X$) is controlling, we have t the expression

(15)

fusion criterion to particle een discussed in connection n on catalyst granules (7). itude criterion defining the onent systems for no mass-realizing the formal kinetics

ressure requirement for the

$< P_{B,eq}$

$P_B = [\text{atm.}]$

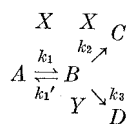
$$\frac{V R^2}{t D} \quad (15a)$$

imum size of catalyst com-diffusivity ($D = 2 \times 10^{-3}$ es/sec. cm^3), as a function partial pressure) which the

acy of a magnitude which is $R = 10^{-4}$ cm. = 1μ can ate can be produced with a

olystep reactions may easily

becomes



(scheme IX)

1. Changing Catalytic Strength of the Intercepting Catalyst Component

Let us examine a typical and relevant example of such a reaction scheme quantitatively, where $(k_1/k_1') \ll 1$, i.e., the amount of B produced is very small. It is obvious from an inspection of scheme IX that the rates of production of B and C at any one moment will have the ratio $(dC/dt)/(dB/dt) = k_2/k_3$, and thus the amounts converted to these respective products will stand in that ratio,

$$C(t)/D(t) = k_2/k_3 \quad (16)$$

which determines the selectivity in a simple manner. The total conversion ϵ is easily seen to be

$$\epsilon = 1 - \exp(-k_E \tau); \quad k_E = \frac{(k_2 + k_3)k_1}{k_1' + k_2 + k_3} \quad (17)$$

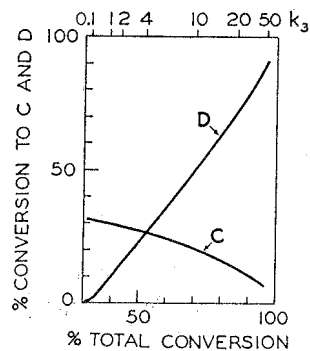


Fig. 4. Selectivity dependence (conversions to products C and D) of reaction scheme IX on the magnitude of the rate constant k_3 ; for $k_1 = k_2 = 4$, $k_1' = 100$, $\tau = 10$.

2. Changing Catalytic Strength of the Intercepted Catalyst Component

Suppose it is desired to make the species D of scheme IX, and a given catalytic activity k_3 is available for the intercepting component. If now the

catalytic strength of the intercepting component is responsible for both as for the competing step k_2 .

Figures 5a and 5b show two IX and the formulas above, for here the catalytic strength of the

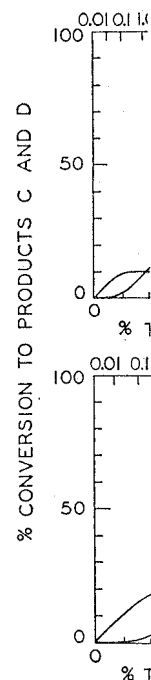


Fig. 5. Selectivity dependence (conversions to products C and D) of reaction scheme IX on the magnitude of the rate constant k_3 ; for $k_1 = k_2 = 4$, $k_1' = 100$, $\tau = 10$.

the constant ratio $k_1/k_1' = 1/10$ as indicated. The conversion maximum as the strength of the selectivity thereafter changes in due course at the maximum, as well as occurs, depend on the catalyst strength (Figs. 5a and 5b).

catalytic strength of the intercepted catalyst system X is varied, we obtain a noteworthy result for the course of the reaction because the X catalyst component is responsible for both the necessary generating step k_1 as well as for the competing step k_2 .

Figures 5a and 5b show two examples calculated from the same scheme IX and the formulas above, for $k_3 = 1$ and for $k_3 = 2$, respectively; since here the catalytic strength of the entire X -system is varied, we have used

Catalyst Component

of such a reaction scheme at of B produced is very IX that the rates of pro- the ratio $(dC/dt)/(dB/dt)$ respective products will

(16)

er. The total conversion

$$\frac{k_2 + k_3}{k_2 + k_3} k_1 \quad (17)$$

and with $A_0\epsilon(t) = C(t) +$ very small amount of B trace the effect of intro- X -catalyst system the st Y having a rate con-

g. 4 shows a plot of the product vs. the total con- of the magnitude of the yst when introduced into catalyst system X , having $k_2 = 4$, $k_1' = 100$, for a). Thus the new product units increasing with the constituting an increas- on the original reaction.

Catalyst Component

scheme IX, and a given ng component. If now the

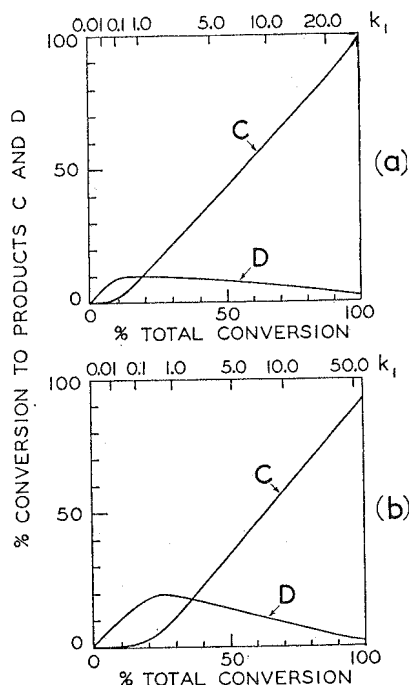
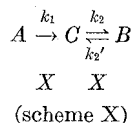


FIG. 5. Selectivity dependence (conversions to products C and D) of reaction scheme IX on the magnitude of the rate constants of catalyst component X at constant Y -component strengths $k_3 = 1$, and $k_3 = 2$; for $k_1/k_1' = 1/100$, $k_2/k_1 = 1$, $\tau = 10$.

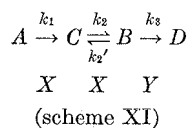
the constant ratio $k_1/k_1' = 1/100$ and $k_2/k_1 = 1$, with $\tau = 10$, and k_1 varying as indicated. The conversion to D increases and proceeds through a maximum as the strength of the X -system is increased, and the catalytic selectivity thereafter changes in favor of product C . The amount of D producible at the maximum, as well as the total catalyst conversion at which it occurs, depend on the catalyst strength k_3 of Y that is available (compare Figs. 5a and 5b).

3. "Coupling" through a Side Product

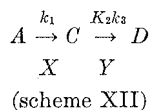
It is important to recall (see Section II,B,2 and II,B,3) the limitation we must ascribe to the meaning of "quasi-intermediates" as to their being true intermediates in the monofunctional X-system. We must recognize that similar "coupling" of a second catalytic system (Y) to a previously monofunctional system can be attained where the latter system can be pictured as one generating a low level *side-product*



The situation may arise reasonably often that, for reasons of an unfavorable thermodynamic equilibrium ($k_2/k_2' \ll 1$), B is produced at a very small concentration level which may remain undetected, or whose potentially profound significance is not easily suspected. Yet the magnitude of the individual rate constants k_2 and k_2' may well be so great that the reaction can be made to proceed rapidly through B to a new product if a "sink" in the form of an adequately large rate constant for the consumption of B is provided by a new catalyst component;



In fact, if the rate constants k_2 and k_2' are adequately fast the product B will at any time be a constant fraction of the material C and the behavior of this system will be easily recognized as equivalent to that of



where K_2 is the equilibrium constant $K_2 = k_2/k_2'$ in scheme XI.

If, therefore, for a given monofunctional catalyst subject to scheme X with certain k_1 , a Y-component is added, draining of C into the new product D can occur in the manner of a consecutive reaction (scheme XII) for which kinetic behavior has been variously analyzed (e.g., in ref. 10). For example, the product compositions of C and D for $k_1 = 0.2$, $\tau = 10$, and variable ($K_2 k_3$) are plotted in Fig. 6.

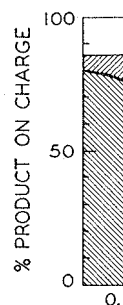


Fig. 6. Relative product variation when the effective second step rate

Thus a low-level "side product" can arise in polyfunctional catalysis to arise from the properties of a quasi-intermediate.

4. Applicability of the Diffusion Criterion

The main difference between this situation and the previously discussed one is in the fact that here the single intermediate becomes the intermediate in the new system. The Y- and the X-system occur in parallel. The intermediates between X-sites and Y-sites must apply or the diffusion criterion must be applied. The criterion, of form

F. THERMODYNAMICS

1. Obtaining an Activity Sequence

The intimacy criterion about a reaction rate, and a quantity that presents a link between

* Note that circumstances may arise that are not than expressed by (15); namely, with the maximum possible concentration of the intermediate, that is $B_{\max} = A[k_1/(k_1' + k_2)]$ is a minimal requirement.

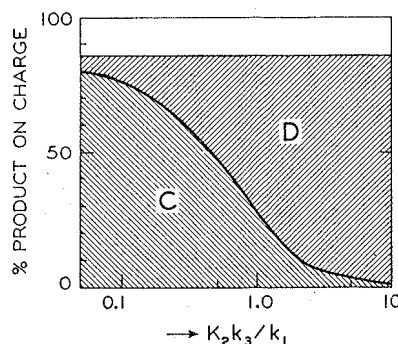


FIG. 6. Relative product variation (C and D) in consecutive reaction of scheme XII when the effective second step rate constant (K_2k_3) changes; $k_1 = 0.2$, $\tau = 10$.

Thus a low-level "side product" may play a role in allowing polystep and polyfunctional catalysis to arise, in that this side-product possesses the potential properties of a quasi-intermediate.

4. Applicability of the Diffusion Criteria

The main difference between the cases discussed in this section on selectivity and the previously discussed case of a simple polystep reaction resides in the fact that here the single component which generates the species that becomes the intermediate in the polyfunctional composite *can* itself generate a distinct product species with appreciable yield. Since the coupling between the Y- and the X-system occurs in any event through mass-transport of intermediates between X-sites and Y-sites, the diffusion criteria already discussed must apply or the kinetic schemes which accomplish "interception" or selectivity control will not be physically and effectively accomplished. The criterion, of formula (15) should be satisfied.*

F. THERMODYNAMICS OF THE POLYSTEP RATE PROCESS

1. Obtaining an Activity Sequence

The intimacy criterion above (15, 15A) involves physical parameters, a reaction rate, and a quantity based on *thermodynamic* equilibrium. It thus presents a link between rate process variables and thermodynamics.

* Note that circumstances may arise where the intimacy requirement is *more* stringent than expressed by (15); namely, when $k_2 > k_1'$ in scheme IX. Then, (15) should contain the maximum possible concentration B_{\max} in place of the equilibrium concentration B_{eq} , that is $B_{\max} = A[k_1/(k_1' + k_2)]$, since $B_{\max} < B_{\text{eq}} = A(k_1/k_1')$. In such a case (15) is a minimal requirement.

It will be instructive therefore to discuss the polystep kinetics in the light of thermodynamics.

For the successive species involved in a polystep conversion, we can examine the successive changes in free energy as we pass from reactants to products. Figure 7 shows this by a plot of positions of the standard free

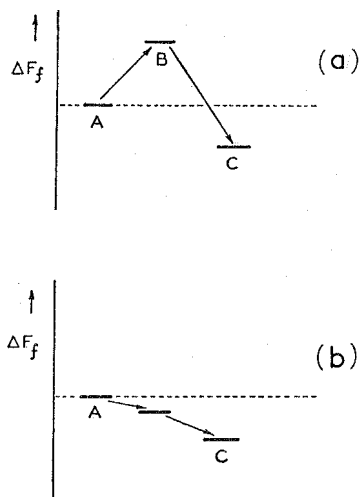


FIG. 7. Thermodynamics of the (a) nontrivial and of the (b) trivial polystep reaction.

energies of formation of the species of each step in the two-step reaction, scheme VIII.

Of course, the over-all change $\Delta F_{A \rightarrow C}$ must be favorable, i.e., in most cases negative. The requirement for nontriviality, as discussed in Section IV, translates itself into the requirement that for the nontrivial case, $\Delta F_{f,B}$ must lie *above* $\Delta F_{f,A}$, as shown by Fig. 7a, while Fig. 7b represents the trivial consecutive reaction.

Thus, the step $\Delta F_{A \rightarrow B}$, to be nontrivial, *must* be positive; and the intimacy criterion (15, 15A) indicates *how* positive it *may* be for certain physically attainable conditions. For a simple monomolecular transformation, as the intermediate step, we have

$$P_{B_{eq}} = P_A \exp(-\Delta F_{A \rightarrow B}/RT)$$

and therefore (15A) becomes

$$\Delta F_{A \rightarrow B} < RT \ln \left[4.4 \times 10^{-5} \left(\frac{273}{T} \right) DP_A / \frac{dN}{dt} R^2 \right]$$

It is interesting to plot the ΔF for the intermediate step, which is still permissible for

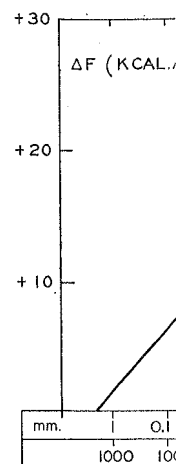


FIG. 8. Maximum permissible ΔF for the intermediate.

heterogeneous polyfunctional for the typical physical magni

2. Obtaining Selectivity

In the case of "interception" of the reaction path from A to B to C is diverted to a new path through action of an additional reagent, the thermodynamics of the situation is represented by Fig. 9.

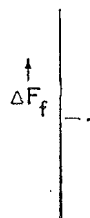


FIG. 9. Thermodynamics of selectivity.

tory, but it is particularly noteworthy that the product D may be made at a rate which is not limited by the properties are such that C is not in equilibrium $C \rightleftharpoons D$ would not be a problem. This is a very useful

It is interesting to plot the magnitude of ΔF for the "initiating" reaction which is still permissible for certain reasonable size parameters R of a

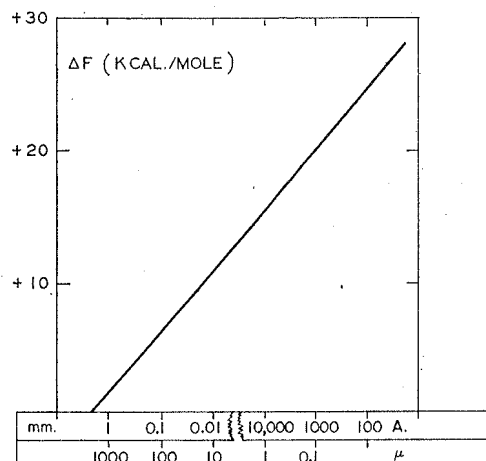


FIG. 8. Maximum permissible ΔF for the initiating reaction ($A \rightarrow B$) which produces the intermediate.

heterogeneous polyfunctional catalyst system. Figure 8 shows such a plot, for the typical physical magnitudes as employed previously above.

2. Obtaining Selectivity

In the case of "interception" (scheme IX), a monofunctional reaction A to B to C is diverted to a new product D by provision of a new reaction path through action of an additional catalyst component. The thermodynamics of the situation is represented by Fig. 9. The figure is self-explanatory.

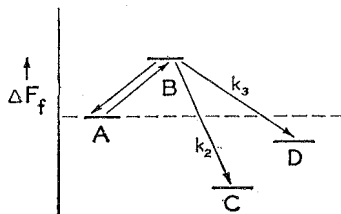


FIG. 9. Thermodynamics of selectivity in polystep reactions; compare with scheme IX.

tory, but it is particularly noteworthy that in a finite contact operation the product D may be made at the expense of C even though the thermodynamic properties are such that C is more stable than D , i.e., even though the direct equilibrium $C \rightleftharpoons D$ would not enable any appreciable conversion to occur from C to D . This is a very useful consideration as it enables one to show that,

$$DP_A \left/ \frac{dN}{dt} R^2 \right]$$

upon introduction of the second catalyst component, the occurrence of the new product D could not have arisen through further conversion of the previous product, in the order $A \rightarrow C \rightarrow D$.

III. The Technique of Physically Mixed Catalyst Components

The simplest direct method for testing the cooperative action of catalyst components consists of a comparison of conversion results between experiments where only catalyst particles of type X , only of type Y , and where a loose mixture of the same amounts of X and Y particles have been placed into the reaction zone, under otherwise similar contact conditions. Polystep action is then indicated if the extent of reaction in the latter case is seen to exceed the sum of the conversions in the two single component contact runs.

In a given experiment the observed effect may, of course, be immeasurably small due to diffusion effects discussed in Section II,D. In that case, a sufficient lowering of the *component* particle size may uncover the effect. If the effect can be thus demonstrated to exist, *a study of the dependence of catalytic effectiveness on the component particle size can be used to yield information concerning the magnitude of vapor pressure of the intermediates*, in accordance with Section II,D,3.

In an ordinary static bed reactor vessel particles with diameters down to about 5×10^{-2} cm. = 500μ can often be used without excessive plugging or pressure drop. For smaller size component particles static bed operation can be achieved by forming larger pellets from the mechanical component mixtures. Conventional pressure-pelletizing or extrusion techniques can be used. In the author's researches, pressure pelletizing the mechanical mixture in the dry state without added binding agents has been employed to avoid aqueous ionic migration of materials, or interaction with third component materials. While such a procedure may result for some materials, in pellets which are relatively weak mechanically, it is usually adequate enough for research experimentation where no large demands exist for mechanical strength.

For porous oxide particles a size-range down to about 60μ diameter can be obtained by conventional crushing and grinding techniques. Smaller particle sizes are obtained by conventional ball-milling, thus reaching a size range of the order of $1-5\mu$.

Thorough mixing of components before pelletizing is, of course, an important prerequisite, since otherwise the size of heterogeneous *domains* becomes subject to the diffusion criterion (15) (see Section II,D,3). Such mixing can be achieved by co-ball-milling, or by use of a Waring blender. In research preparations the latter method was preferred in order to preserve strictly mechanical intermingling and minimize spot heating at interfaces. Homogeneity was checked under an optical microscope.

In studies of dual-function catalysts, many advantages, two of which are independent preparation of catalyst components. Preparation can be made of catalysts with platinum activity without the acidic properties of the support, a matter of concern in certain cases. A component's relative activity is then perfectly known and controlled in admixture with the other component.

IV. Some Major

A number of hydrocarbons and Donaldson (10), Heil (12) to be catalyzed by separate platinum or nickel, has been found. These include the isomeric naphthalene rings, and the

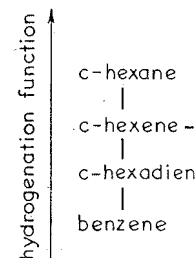


Fig. 10. Formal reaction conversion, after Mills *et al.* (13).

Mills *et al.* (13) propose that the reaction proceeds through olefinic intermediates by Fig. 10 for the C_6H_{12} separate catalytic function on the olefinic intermediate on a hydrogenation activity.

* We do not consider the products (methylcyclopentane — reproduce it in accordance with any rate—involved in the reaction).

t, the occurrence of the other conversion of the

Catalyst Components

relative action of catalyst results between experiments of type Y, and where articles have been placed under conditions. Polystep in the latter case is seen to component contact runs. of course, be immeasurable on II,D. In that case, a study of the dependence of size can be used to yield nature of the intermediates,

with diameters down to about excessive plugging. Besides static bed operation, mechanical component isolation techniques can be the mechanical mixture been employed to avoid with third component some materials, in pellets adequately enough for as exist for mechanical

about 60 μ diameter can be using techniques. Smaller milling, thus reaching a

izing is, of course, an heterogeneous domains (see Section II,D,3). Such use of a Waring blender. preferred in order to pre-vent spot heating at inter-microscope.

In studies of dual-functional catalysis the mixed catalyst technique has many advantages, two of which are mentioned. (1) It allows separate and independent preparation of each component; for example, a platinum preparation can be made in any manner desired in order to obtain a certain platinum activity without regard to what such procedures might do to the acidic properties of the oxide base, this interdependence always being a matter of concern in conventional direct impregnation techniques. (2) A component's relative activity contribution can be flexibly varied in a perfectly known and controllable manner by simply varying its bulk amount in admixture with the other.

IV. Some Major Polystep Reactions of Hydrocarbons

A number of hydrocarbon transformations have been shown by Haensel and Donaldson (10), Heinemann *et al.* (11), and by Ciapetta and Hunter (12) to be catalyzed by solid catalysts in which a transition metal, notably platinum or nickel, has been combined with an "acidic" oxide carrier substance such as, for example, silica-alumina, or halogen containing alumina. These include the isomerization of paraffins, the hydroisomerization of naphthene rings, and the hydrogenative cracking of paraffins.

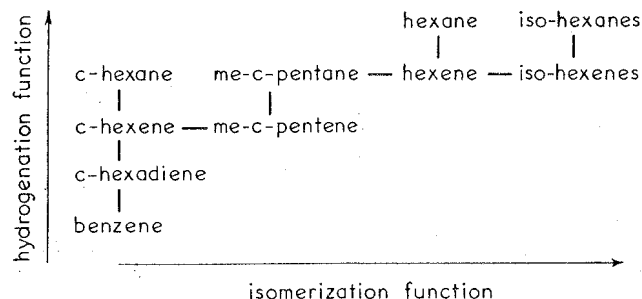


FIG. 10. Formal reaction path representation for dual functional C_6 -hydrocarbon conversion, after Mills *et al.* (13).

Mills *et al.* (13) proposed formal reaction schemes in which conversion proceeds through olefinic reaction intermediates, such as the one illustrated by Fig. 10 for the C_6 -hydrocarbons.* They introduced the concept of separate catalytic functions, in terms of an isomerization activity—operative on the olefinic intermediate—associated with the acidic oxide base and a hydrogenation activity associated with platinum. Ciapetta and Hunter

* We do not consider the particular link between the cyclic and the aliphatic structures (methylcyclopentane \rightarrow hexene) as properly presented by this diagram. We reproduce it in accordance with the authors' picture since this reaction step is not—at any rate—involved in the reactions here discussed.

(12) in their work on paraffin isomerization proposed that "the isomerization activity of these catalysts is due to compound formation between the nickel and hydrous aluminum silicate," thus forming a special active catalyst "complex."

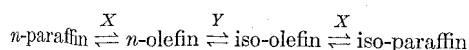
Mills *et al.* (13) proposed that (see Fig. 10) "in order to travel to a compound in a diagonal position, it is necessary to transfer on the catalyst surface from one site to another." Thus the concept of the "dual functional" hydrocarbon conversion catalyst with distinctly different sites became clearly introduced.

In the author's laboratory, extensive studies were undertaken not only to examine the reaction schemes proposed by Mills *et al.*, but specifically to test the feasibility of catalytic cooperation by chemically unconnected, i.e., physically separate, catalytic components, wherein the intermediates are true gas phase species coupling the catalyst components through mass transport following the classical laws of gaseous diffusion, in line with the principles and characteristics discussed in the preceding sections. Experimental work that makes use of physically distinct catalytic materials or components constitutes the most direct route to the testing and study of true polystep reaction mechanisms.

The feasibility of coupling through the diffusion process was briefly reported by Weisz (14). Experimental evidence of the cooperative action of catalyst mixtures was mentioned by Mills (15) and Weisz (16) at the First International Congress on Catalysis, and brief reports have appeared by Weisz and Swegler (17), Hindin *et al.* (18), and Weisz (19).

A. REACTIVITY FOR ISOMERIZATION OF PARAFFINS

The reaction*



has been studied using the mixed catalyst technique.

The "acidic" solid catalysts, such as silica-alumina are very active for the conversion of olefins to skeletal isomers. Evidence for such high reactivity, at relatively low temperatures, can be found, for example, in the early work of Egloff *et al.* (20), and of Greensfelder and Voge (21).

Over conventional silica-alumina cracking catalyst (422 m.²/g. surface area, 11% Al₂O₃) such as has been used in the author's laboratory in some of the mixed particle researches to be described below, contacting 1-hexene with a residence time of 3.5 sec. at atmospheric pressure leads to 43% conversion to skeletal isomers at 300°C (17).

* In this and following reaction schemes participation of hydrogen will be silently assumed and not explicitly shown. The schemes trace the course of the hydrocarbon structures.

With such a catalyst available, we hope to find that mechanism, catalyst, an over-all paraffin

1. Simple Demonstration Test

The isomerization of *n*-hexane, the additivity effect of fair reactor, even in atmospheric pressure, 0.8–1.5 mm. diameters of a minia (Y). In a typical example, chloroplatinic acid impregnated silica (tetraethylsilicate), drying bearing 0.55 wt. % of platinum catalyst described above. The hexanes observed when the catalyst components alone, takes place at 373°C, at a 1:1 hydrogen at a 5:1 molar ratio

Polystep Hexane Isomerization

Catalyst charge

10 cm.³ of silica/Pt
10 cm.³ of silica-alu
Mixture of 10 cm.³
10 cm.³ of Y

The successful interaction from these results of a simple

The thermodynamics of the reaction indicates a maximum attainable depending on whether the double-bond isomer like 1-hexene or double bond isomers at full the observed action of polystep reaction of Section II, C, and re simplicity, would even lend classroom demonstration, sir tially immediately with sim

The criterion (15) can be merization demonstrated b

With such a catalyst available for the olefin isomerization step one may hope to find that mechanical combination with a (de-) hydrogenative catalyst, an over-all paraffin isomerization may be accomplished.

1. Simple Demonstration Tests with *n*-Hexane

The isomerization of *n*-hexane is indeed demonstrable by simply showing the additivity effect of fairly large particle mixtures "poured" into the reactor, even in atmospheric pressure operation with a particle size of 0.8–1.5 mm. diameters of a platinum-bearing material (*X*) and silica-alumina (*Y*). In a typical example, the *X*-catalyst is obtained by aqueous chloroplatinic acid impregnation of a pure silica (obtained from hydrolysis of tetraethylsilicate), drying and calcination in air at 450°C for 1 hr., and bearing 0.55 wt. % of platinum; the *Y*-catalyst is the commercial cracking catalyst described above. Table I below illustrates the conversion to iso-hexanes observed when the reactor is charged with either of the two catalyst components alone, or with a loose mixture of both. The operation takes place at 373°C, at a feed-rate of 17.2 g. of *n*-hexane per hour, with hydrogen at a 5:1 molar ratio of hydrogen to *n*-hexane.

TABLE I
Polystep Hexane Isomerization on Coarse Catalyst Mixtures

Catalyst charge to reactor	Wt. % Conversion to iso-hexanes
10 cm. ³ of silica/Pt (<i>X</i>)	0.9
10 cm. ³ of silica-alumina (<i>Y</i>)	0.3
Mixture of 10 cm. ³ of <i>X</i> and 10 cm. ³ of <i>Y</i>	6.8

The successful interaction of the two catalyst components is apparent from these results of a simple "poured" and loose particle mixture.

The thermodynamics of the *n*-paraffin \rightleftharpoons *n*-olefin step (see Fig. 1) indicates a maximum attainable first step conversion of between 0.04 and 0.6%, depending on whether dehydrogenation occurs to predominantly one double-bond isomer like 1-hexene, as one extreme case, or possibly all double bond isomers at full equilibrium concentration, as the other. Thus the observed action of polyfunctional coaction is not trivial, by the definition of Section II,C, and represents a demonstration which in view of its simplicity, would even lend itself—like others to be discussed below—to classroom demonstration, since product spectra can now be displayed essentially immediately with simple vapor chromatographic techniques.

The criterion (15) can be applied to show that the rate of paraffin isomerization demonstrated by the simple experiment above represents a

heavily mass-transport inhibited rate, far below that which could be potentially attained at smaller component particle size. From the observed conversion (Table I) and the *n*-hexane feed-rate, the rate per-unit-volume of catalyst component calculate to be $dN/dt = 0.5 \times 10^{-6}$ moles/sec./cm.³. The maximum possible concentration of olefin intermediates was stated above to be 0.6% of the paraffin vapor pressure and is thus found to be about $[B_{eq}] = 2.4 \times 10^{-8}$ moles/cm.³. The effective diffusivity of the silica-alumina material used in the author's laboratory has been determined independently by methods previously described (8, 22), and is $D_{eff} = 2 \times 10^{-3}$ cm.²/sec. Thus, with an average particle size of $2R = 6 \times 10^{-2}$ cm., one obtains

$$\Phi = \frac{dN}{dt} \frac{1}{[B_{eq}]} \frac{R^2}{D} \approx 36$$

i.e., a number far above unity and which we call Φ . As pointed out by Weisz and Prater (ref. 22, p. 167), it is possible to obtain the magnitude of the catalyst effectiveness factor η from the magnitude of Φ . In fact, when $\Phi \gg 1$, one can show that $\eta \approx 1/\Phi$, so that we get $\eta \approx 0.03$ for the experiment, i.e., only 3% of possible reactivity was realized. (This is an upper limit since the maximum olefin vapor pressure including all theoretically possible double-bond isomers was assumed.)

2. Demonstration of the Intimacy Requirement with *n*-Heptane

The applicability of the intimacy criterion has been demonstrated (19) in a series of tests on *n*-heptane isomerization under conventional operating conditions, i.e., at elevated hydrogen partial pressure where catalyst deactivation is minimized. The reaction was examined over mechanically distinct but mixed particles of X (Pt-bearing particles) and Y (silica-alumina) of varying particle size R (equal for both types of particles) in 50-50 volume proportion as well as over single type catalyst in the reaction zone. The reaction conditions provided a partial pressure of *n*-heptane of 2.5 atm., of hydrogen of 20 atm., and a residence time of 17 sec.

Figure 11 shows conversion to iso-heptanes to be negligible for (0.5 wt. %) platinum supported on activated carbon (Pt/C) as the only catalyst, and also for (0.4 wt. %) platinum on silica-gel (Pt/SiO₂). No detectable conversion was obtained with silica-alumina. A mechanical mixture of either of the Pt-bearing particles with silica-alumina of about 150 m.²/g. surface area, both in millimeter diameter particle size (1000 μ), immediately resulted in appreciable isomerization (\otimes SiAl with Pt/C; \oplus SiAl with Pt/SiO₂). Isomerization increases rapidly for smaller component particle sizes, of 70 μ and 5 μ diameters. It approaches the performance of a silica-alumina that has been directly impregnated with platinum, and which has

the same total silica-alumina; *n*-heptane production vs. conversion. The close approach to diffusion-controlled rates for small particle sizes below 100 μ .

The conversions in this case are at least to the mono-methyl heptanes.

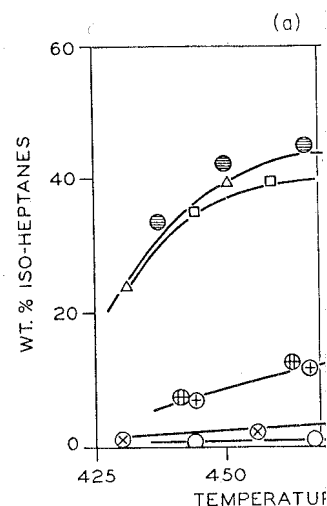


FIG. 11. Isomerization of *n*-heptane over component particles: (a) conversion vs. component particle diameter.

functional catalytic isomerization. The effect of particle size from the intimacy criterion is brought into consideration the appropriate conversion.

For an integral reactor, the rate equations—lead to an expression for the overall reaction rate, with $[A]$ being the reactant concentration.

$$\frac{dN}{dt}$$

where ϵ and ϵ_{eq} are the observed and equilibrium overall reaction rates.

Since we can write, for the overall reaction

$$\Phi$$

that which could be potentially. From the observed conversion rate per-unit-volume of 5×10^{-6} moles/sec./cm.³.

intermediates was stated and is thus found to be effective diffusivity of the catalyst has been determined and (8, 22), and is $D_{\text{eff}} =$ particle size of $2R = 6 \times 10^{-2}$

call Φ . As pointed out by to obtain the magnitude of magnitude of Φ . In fact, when get $\eta \approx 0.03$ for the experiment realized. (This is an upper including all theoretically

with *n*-Heptane

as been demonstrated (19) under conventional operating pressure where catalyst deactivated over mechanically disintegrated and Y (silica-alumina) particles) in 50–50 volume in the reaction zone. The of *n*-heptane of 2.5 atm., of 7 sec.

to be negligible for (0.5 wt. Pt/C) as the only catalyst, 1 (Pt/SiO₂). No detectable

A mechanical mixture of alumina of about 150 m.²/g. particle size (1000 μ), immediately with Pt/C; \otimes SiAl with smaller component particle the performance of a silica-platinum, and which has

the same total silica-alumina surface area in the reactor (\otimes). A plot of isoheptane production vs. component particle size, at 468°C, Fig. 11b shows the close approach to diffusion-uninhibited performance for component particle sizes below 100 μ .

The conversions in this operation approach equilibrium conversion (at least to the mono-methyl hexanes, which are the major products in dual

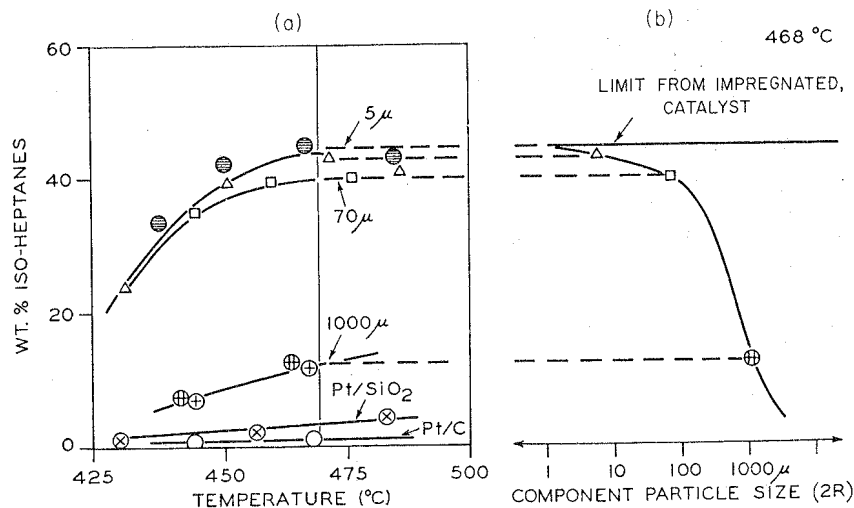


FIG. 11. Isomerization of *n*-heptane over mixed component catalyst, for varying size of the component particles: (a) conversion vs. temperature; (b) conversion at 468°C vs. component particle diameter.

functional catalytic isomerization), near 470°C. Calculated estimates of particle size from the intimacy requirement can be made, but must take into consideration the approach to equilibrium in the range of operating conversion.

For an integral reactor, conventional derivations—for first-order reactions—lead to an expression for $(dN/dt)/(1/[A])$ anywhere along the reactor, with $[A]$ being the reactant concentration

$$\frac{dN}{dt} \frac{1}{[A]} = 1/\tau \ln \frac{1}{1 - \epsilon/\epsilon_{\text{eq}}} \quad (18)$$

where ϵ and ϵ_{eq} are the observed and the equilibrium conversions of the over-all reaction.

Since we can write, for the intimacy criterion (15)

$$\Phi = \frac{dN}{dt} \frac{1}{[A]} \frac{[A]}{[B_{\text{eq}}]} \frac{R^2}{D} < 1$$

we can also write the criterion [with (18)] as

$$\Phi = \frac{[A]}{[B_{eq}]} \frac{R^2}{D} \frac{1}{\tau} \ln \frac{1}{1 - \epsilon/\epsilon_{eq}} < 1 \quad (19)$$

With this we can calculate the requirements at, say, 90% approach to equilibrium, corresponding to 40% conversion to iso-heptanes in Fig. 11. The ratio $[A]/[B_{eq}]$ calculated from the thermodynamics of the paraffin-olefin equilibrium calculates to between 1 and 4×10^3 . We have $\tau = 17$ sec., $D = 2 \times 10^{-3}$ cm.²/sec., $\epsilon/\epsilon_{eq} = 0.9$, from which we obtain

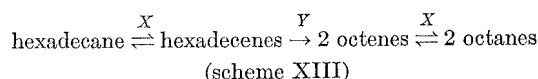
$$\Phi \approx (7 \dots 30) \times 10^4 R^2$$

and thus for $\Phi \approx 1$, we obtain the size magnitude $R \sim 20 \dots 40\mu$, in good agreement with the observations.

The nature of the intimacy requirement is thus well demonstrated experimentally.

B. REACTIVITY FOR HYDROCRACKING OF PARAFFINS

A side reaction of paraffin isomerization is that of hydrogenative cracking to lower molecular weight paraffins. Besides hydrogenolysis of hydrocarbons, which we visualize as occurring on metal catalyst sites alone, polystep hydrocracking according to the scheme exemplified by



can be shown to proceed readily when both Pt-sites (X) and acidic sites (Y) such as of silica-alumina can coact via vapor phase diffusion, in a polystep reaction sequence.

Heinemann *et al.* (11) showed that the hydrogenative cracking of heptane on a dual-functional catalyst leads to butane as a predominant product indicating prevalence of "center-cracking," which recalls an acid-catalyzed cracking activity. Myers and Munns (23) presented evidence for the existence of the dual-functional reaction path for hydrocracking leading to center-cracked products, and for a second and distinct mechanism of hydrogenolysis involving the metal sites alone, the latter leading to bond rupture probabilities equally large towards the ends of *n*-paraffins. From comparisons on *n*-pentane, *n*-hexane, and *n*-heptane, they indicated that the dual-functional hydrocracking mechanism becomes increasingly important with greater molecular weight of the paraffin.

1. Demonstration of the Hydrocracking of Paraffins

Work by Weisz and Swegler has shown the dual-functional (scheme XIII) hydrocracking activity to increase so rapidly with molecular weight, that

with *n*-C₁₂H₂₆, or *n*-C₁₆H₃₄, dual-functional hydrocracking in a spherical pressure reactor. The demonstration of the nature of the dual-functional catalyst components, a comparison of the components. The components are silica-alumina and Pt-carbon. The measurements are at partial pressures of 0.25 atm and 3 sec. residence time. The results show that with only silica-alumina, with a 50/50 volume mixture into the reactor space. Reaction (mediate) cracking is so high that the reaction is limited through vapor phase component diffusion inhibition in relative

Polystep Hydrocracking of Paraffins on Co

Catalyst

Silica-alumina
Pt-carbon
Pt-carbon + Silica-alumina

^a E.P. = distillation end-point temperature

Higher reactivities are attained with smaller catalyst size. Such mixed catalysts were prepared from particles of two components: 1) 420 m.²/g. silica-alumina cracked in a 3/16" cylindrical pellets. Under conditions above, but at still lower temperatures (to products boiling below 100°C) runs each of 75 min. duration (flow).

The high reactivity of an acid catalyst is evident for the cracking of the higher paraffins by previous work (20, 21). It is a direct result of our work (19), when c

with $n\text{-C}_{12}\text{H}_{26}$, or $n\text{-C}_{16}\text{H}_{34}$, a striking and simple demonstration of the dual-functional hydrocracking mechanism can be made in a simple atmospheric pressure reactor. The method is analogous to that used in the demonstration of the nature of n -hexane isomerization, involving tests with single catalyst components, and with a loosely poured mixture of both components. The components are identical to those used in the n -hexane experiments. The measurements are made at 370°C reactor temperature, at partial pressures of 0.25 atm. of hydrocarbon and 0.75 atm. of hydrogen and 3 sec. residence time. Table II below shows conversions observed with only silica-alumina, with only platinum on activated carbon, and with a 50/50 volume mixture of both particles simply poured together into the reactor space. Reactivity of high molecular weight olefin (intermediate) cracking is so high that a high degree of conversion is attainable through vapor phase component interaction, even with the high degree of diffusion inhibition in relatively large component particles.

TABLE II

Polystep Hydrocracking of High Molecular Weight Paraffins on Coarse Mechanical Catalyst Mixtures

Catalyst	Particle size (mm.)	Conversion (%)	
		$n\text{-C}_{12}\text{H}_{26}$ (to 175°C. E.P. ^a)	$n\text{-C}_{16}\text{H}_{34}$ (to 275°C. E.P. ^a)
Silica-alumina	0.8-1.4	2.7	2.1
Pt-carbon	0.8-1.4	4.0	2.5
Pt-carbon + Silica-alumina	0.8-1.4	13.2	36.5

^a E.P. = distillation end-point to define products.

Higher reactivities are attained by decreasing the component particle size. Such mixed catalysts were made by mechanically mixing 50 to 100 μ particles of two components: Pure silica bearing 0.7 wt. % of platinum, and 420 m.²/g. silica-alumina cracking catalyst, and compressing to 3/16" \times 3/16" cylindrical pellets. Under operating conditions identical to the tests above, but at still lower temperature, 358°C., n -dodecane gave the conversions (to products boiling below 175°C.) of Table III, in seven successive runs each of 75 min. duration (each interrupted by one-half hour hydrogen flow).

The high reactivity of an acidic solid such as the silica-alumina component for the cracking of the high molecular weight *olefin* has been indicated by previous work (20, 21). It was demonstrated for the particular conditions of our work (19), when dodecene-1 was passed over the silica-alumina

$$\frac{1}{\epsilon_{\text{eq}}} < 1 \quad (19)$$

its at, say, 90% approach to n to iso-heptanes in Fig. 11. Dynamics of the paraffin- and 4×10^3 . We have $\tau = 17$ m which we obtain

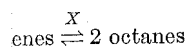
$$0^4 R^2$$

ide $R \sim 20 \dots 40\mu$, in good

thus well demonstrated experi-

ING OF PARAFFINS

hat of hydrogenative cracking
hydrogenolysis of hydrocar-
l catalyst sites alone, polystep
plified by



Pt-sites (X) and acidic sites
por phase diffusion, in a poly-

rogenative cracking of heptane
ne as a predominant product
which recalls an acid-catalyzed
esented evidence for the exist-
for hydrocracking leading to
l and distinct mechanism of
ne, the latter leading to bond
the ends of n -paraffins. From
-heptane, they indicated that
n becomes increasingly impor-
raffin.

raffins

dual-functional (scheme XIII)
y with molecular weight, that

TABLE III
Hydrocracking $n\text{-C}_{12}\text{H}_{26}$ over Mixed (Silica/Pt and Silica-alumina)
Catalyst at 50 to 100 μ Component Particle Size ($\tau = 3$ sec., 358°C.)

Run	Conversion (wt. %)
1	47
2	47
3	43
4	46
5	42
6	41
7 ^a	46

^a 2 hrs. hydrogen flow at 480°C. prior to run 7.

alone, at atmospheric pressure, 3 sec. residence time, and 330°C., with the results in Table IV below.

Furthermore, the molecular weight distributions of the products from the cracking of dodecene-1 and from the hydrocracking dodecane are characteristically similar. Figure 12 shows approximate carbon number distributions obtained from a run of dodecene-1 cracking over silica-alumina (left

TABLE IV
 n -Dodecene Conversion over Silica-alumina Catalyst ($\tau = 3$ sec., 330°C.)

Catalyst surface area (m ² /g.)	Conversion (%) (to 175°C. E.P. ^a)	Gas production (wt. %)
90	18	—
196	36	—
420	47	3.5

^a E.P. = distillation end-point to define products.

side of Fig. 12) and from the average of three hydrocracking runs of dodecane over the (Pt/carbon + silica-alumina) mixed catalyst (right side of Fig. 12). The product distributions are seen to have the same general character.

Thus these relatively simple experiments demonstrate some basic features of dual-functional hydrocracking. Acidic catalyst, like silica-alumina exhibits a very high activity for the cracking of high molecular weight olefins. The corresponding paraffins can be cracked under similar conditions by providing the olefin as intermediate product through the action of a separate but diffusionally coupled dehydrogenation catalyst component, such as, for example, platinum.

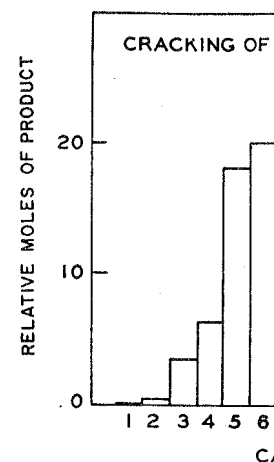


FIG. 12. Relative distribution of products from dodecene-1, and from hydrocracking of dodecane.

2. Hydrocracking and Hydroisomerization

The existence of a mode of dual functional route, for the cracking of high molecular weight olefins, was first reported by Myers and Munns (23), and was later confirmed by the use of the mixed catalyst technique.

By using mechanical mixtures of dual functional catalyst components, the risk of changing the catalyst composition during the reaction is minimized. Such a study was undertaken to compare the results obtained with the dual functional catalyst with those described in Table IV, B, 2 above. The (de)hydrogenation catalyst component was silica-alumina impregnated with platinum, and was treated to remove halogen by 150 m²/g. silica-alumina, 5 μ size, blended, and pelletized.

Figure 13 shows the results of the cracking of dodecene-1 over the dual functional catalyst component of 25/75, 50/50, and 75/25 for isomerization decreases with increasing catalyst component (in spite of increasing catalyst component, at least, of cracking to C₃ and decreases similarly with decreasing catalyst component with the picture that both components are active. However, the results indicate that the products, indicating that the

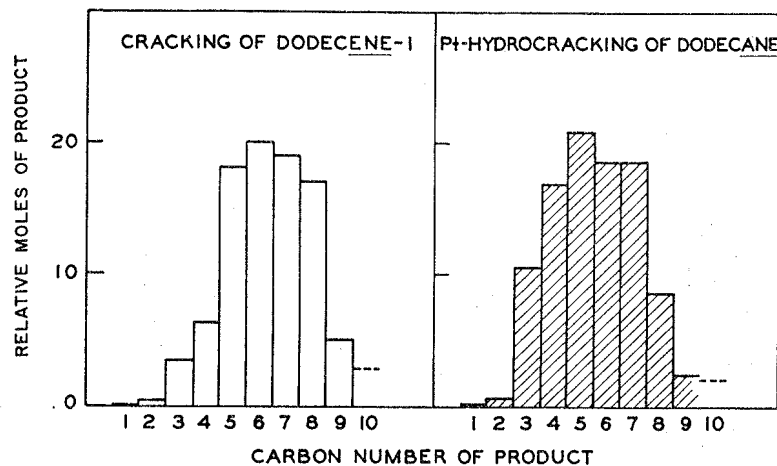


FIG. 12. Relative distribution of carbon number in cracked products from cracking of dodecene-1, and from hydrocracking dodecane.

2. Hydrocracking and Hydrogenolysis

The existence of a mode of hydrogenative cracking other than via the dual functional route, for the light hydrocarbons, as was indicated by Myers and Munns (23), can be demonstrated and substantiated by the use of the mixed catalyst technique.

By using mechanical mixtures of varying proportion of the two catalyst component materials, the relative catalytic strengths can be varied without any danger of changing other qualitative properties of the catalytic sites. Such a study was undertaken with *n*-heptane under operating conditions identical to those described for the *n*-heptane isomerization study in Section IV,B,2 above. The (de-)hydrogenation component consisted of Alcoa F-10 alumina impregnated with 0.4 wt. % of platinum and subsequently steam-treated to remove halogen contents. The acidic component was supplied by 150 m.²/g. silica-alumina cracking catalyst. The components were of 5 μ size, blended, and pelleted in three different volume proportions.

Figure 13 shows the results for the ratios of platinum-component to acid-component of 25/75, 50/50, and 75/25. It will be noted that the activity for isomerization decreases in that order, i.e., with decreasing acidic component (in spite of increasing Pt-component). Similarly the majority, at least, of cracking to C₃ and C₄ paraffins (the "center-cracking" products) decreases similarly with decreasing acidic component. This is consistent with the picture that both reactions are rate controlled by the silica-alumina component. However, the *converse* is true for the appearance of C₁ and C₂ products, indicating that a major portion of these products is obtained

Silica-alumina)
= 3 sec., 358°C.)

e, and 330°C., with the

s of the products from
ing dodecane are charac-
carbon number distribu-
over silica-alumina (left

($\tau = 3$ sec., 330°C.)

Gas production
(wt. %)

3.5

rocracking runs of dode-
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onstrate some basic fea-
alyst, like silica-alumina
f high molecular weight
l under similar conditions
through the action of a
ion catalyst component,

through a different reaction route in which the platinum/alumina component plays the major and rate controlling role.

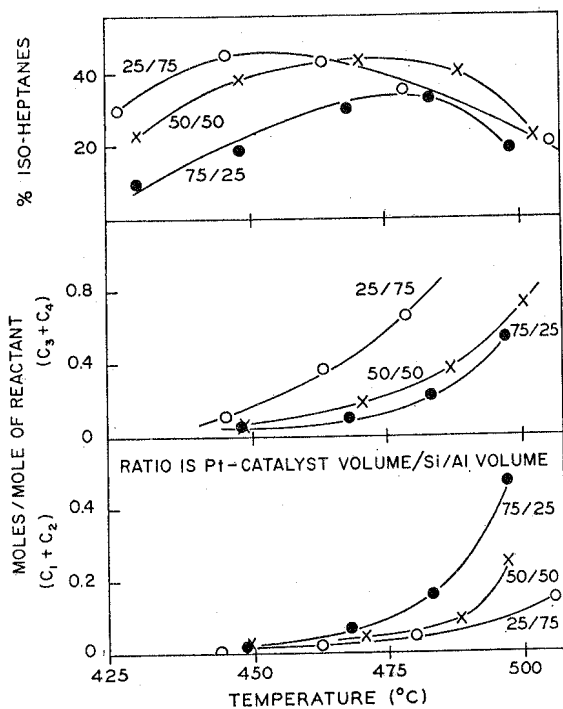
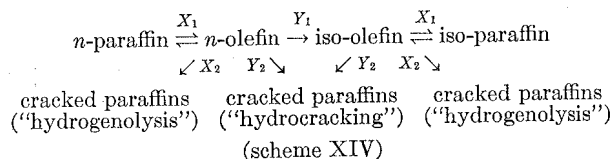


FIG. 13. *n*-Heptane isomerization and hydrogenative cracking over mixed catalysts of varying proportion of platinum and acidic component.

These results and the indications described by Myers and Munns (23) are consistent, therefore, with the following diagram of reaction paths for paraffin hydrocarbons on metal-acidic site dual functional catalysts:



In this scheme, X represents metal sites, and Y represents "acidic" sites. It is suggested that the term "hydrogenolysis" be adopted uniformly to apply to hydrogenative cracking involving the metallic sites alone, while the term "hydrocracking" be used for the dual-functional catalytic conversion. Such terminology would be helpful since the catalytic processes differ both in mechanism as well as nature of products. Hydrogenolysis

leads to relatively indiscriminate breakage of centralized bonds. Provided with acidic activities, cracking catalysts, hydrogenolysis, for paraffin

C. SELECTIVITY

1. Isomerization Selectivity

If we view broadly the picture, we can summarize certain factors involved in some of the factors involved.

Scheme XIV shows the reaction paths with its side-reactions which involve the high activity of the acidic sites (intermediate) olefin isomerization, carbon number to high carbon number, qualitatively in Fig. 14.

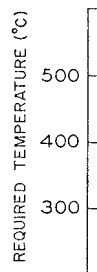


FIG. 14. Qualitative sketch of paraffin hydrogenolysis (on platinum/alumina).

alumina exhibits hydrogenolysis. It depends on the catalyst preparation and paraffin size. Consequently, for light paraffins, the temperature requirements are low to operate under conditions of low pressure.

Thus for light paraffin isomerization, the ratio of rate constants is desired. This implies that the catalyst components are in equilibrium, as discussed in Section II, E, and the component strength to increase

platinum/alumina com-

leads to relatively indiscriminate bond breakage, as compared to preferred breakage of centralized bonds in hydrocracking. When catalysts are provided with acidic activities comparable to those of active conventional cracking catalysts, hydrocracking can be obtained at a level far above hydrogenolysis, for paraffins of carbon number n much greater than seven.

C. SELECTIVITY IN POLYSTEP PARAFFIN REACTIONS

1. Isomerization Selectivity

If we view broadly the past and present work cited and reported above, we can summarize certain observations that lead to an understanding of some of the factors involved in catalytic selectivity of paraffin conversion.

Scheme XIV shows the reaction path of dual functional isomerization with its side-reactions which detract from perfect selectivity. For a given high activity of the acidic component Y , the temperature requirement for (intermediate) olefin isomerization activity drops rapidly as we go from low carbon number to high carbon number paraffins. This is pictured purely qualitatively in Fig. 14. A typical metal component such as platinum-

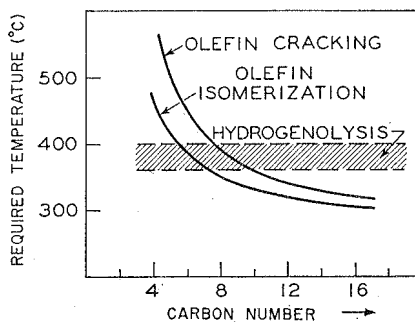


Fig. 14. Qualitative sketch of reactivities for olefin reactions (on acidic catalyst) and paraffin hydrogenolysis (on platinum metal) vs. carbon number of hydrocarbon.

alumina exhibits hydrogenolysis activity at a temperature level which depends on the catalyst preparation but does not vary greatly with n -paraffin size. Consequently, for the isomerization of the lighter paraffin, the temperature requirements (forced upon us by the Y -component) force us to operate under conditions where hydrogenolysis becomes prevalent.

Thus for *light paraffin* isomerization, the selectivity depends importantly on the ratio of rate constants involved in steps Y_1 and X_2 ; i.e., $k_{Y_1}/k_{X_2} \gg 1$ is desired. This implies that relative activities of the two independent catalyst components are involved, and may be controllable in the manner discussed in Section II,E,2. One may reduce k_{X_2} by decreasing X -component strength to increase said ratio. This reduction of strength should

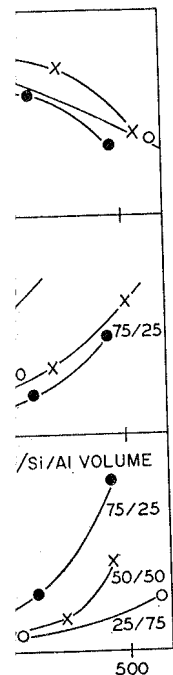


Fig. 13. Cracking over mixed catalysts. The curves show that as the Si/Al volume increases, the cracking activity (X) decreases, with the 75/25 catalyst showing the highest activity and the 25/75 catalyst showing the lowest activity.

by Myers and Munns (23) diagram of reaction paths for dual functional catalysts:

k_1
= iso-paraffin
cracked paraffins
("hydrogenolysis")

Y represents "acidic" sites. s be adopted uniformly to be metallic sites alone, while dual-functional catalytic consequences the catalytic processes of products. Hydrogenolysis

be useful until the generating rate constant k_{X_2} (due to the same catalyst sites) becomes inadequately small. This is aptly demonstrated by a laboratory experiment on *n*-hexane isomerization, by the use of a mixed composite of platinum and acidic catalyst of very high initial platinum activity, which is subsequently progressively lowered by contacting with the catalyst increasing amounts of hydrogen sulfide which lowers platinum activity (X_1 and X_2) alone. Figure 15 shows the changes in effluent product

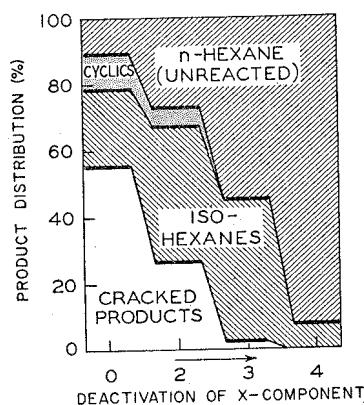


FIG. 15. Observed variation of *n*-hexane isomerization selectivity with degree of activity of the *X*-component in a platinum (*X*) acidic oxide (*Y*) catalyst.

distribution, as 0, 2, 3, and 4 total units of hydrogen sulfide have been contacted with the catalyst, operating at 373°C., at approximately 2.3 sec. residence time, 0.9 atm. of hydrogen and 0.1 atm. of *n*-hexane partial pressure.

Essentially all hydrogenative cracking is seen to have resulted from hydrogenolysis on Pt-sites, and is progressively suppressed by lowering the platinum rate constants with hydrogen sulfide, until further lowering results in quenching of the olefin producing generating step of the dual functional isomerization.

Experimental details. The reaction is carried out in a microcatalytic reactor substantially as described by Kokes *et al.* (24). The catalyst consists of 2.8 g. of a pelleted 1:1 volume mixture of particles of Alcoa F-10 alumina impregnated with 0.6 wt. % of platinum and of 420 m.²/g. silica-alumina cracking catalyst, maintained in hydrogen at a flow rate of 60 cm.³ (S.T.P.)/min. A pulse of 2 cm.³ (S.T.P.) of a 10:1 mixture of hydrogen/*n*-hexane is inserted into the flowing gas stream, passed over the catalyst and through a vapor chromatographic column to record the product spectrum. Metered amounts of gaseous hydrogen sulfide, in units of 1/64 cm.³ (S.T.P.), are introduced into the hydrogen stream passing to the catalyst, in between successive activity tests, for progressive deactiv-

ation of platinum activity. such units of H₂S placed on

The pulse technique provides hydrocarbon charge and all "fresh" platinum activities.

As we consider isomerization of olefin cracking reactions, on the hydrogenolysis reaction becomes more complex. Intrinsically large, the intrinsic characteristic of the reaction represents a problem differing in catalyst component structure.

2. Hydrocracking Selectivity

When the molecular weight is lowered by hydrocracking, products are also encountered two types of operating conditions are required to minimize the Y_2 reactions as less implies that the Y_1 reaction is the isomer distribution towards

One problem is again a matter of now k_{Y_2}/k_{X_2} is to be sufficient selectivity problem is a more of the bond ruptures in the product ratios of this intrinsic

D. REAC

The conversion of cyclohexane reaction which will react with metal oxides. On chromia-alumina, Swegler (25) have demonstrated the occurrence of early diffusional escape of cyclohexane. Prater *et al.* (26) have developed a quasi-intermediate in aromatic compounds although at a smaller concentration. rate constants k_2/k_1 in the series

cyclohexane

for platinum catalysis compounds

(due to the same catalyst
demonstrated by a lab-
by the use of a mixed
ery high initial platinum
wered by contacting with
ide which lowers platinum
hanges in effluent product

ation of platinum activity. Figure 15 indicates the cumulative number of such units of H_2S placed on the catalyst.

The pulse technique provides very brief contacts of the catalyst with hydrocarbon charge and allows measurements to be made at the very high "fresh" platinum activities.

As we consider isomerization of paraffins with *larger carbon number*, the olefin cracking reactions, on Y_2 , become of increasing importance relative to the hydrogenolysis reaction X_2 (see Fig. 14), and the selectivity problem becomes more complex: In addition to the control of k_{Y_1}/k_{X_2} to be sufficiently large, the intrinsic ratio k_{Y_1}/k_{Y_2} should be large. The latter is an intrinsic characteristic of the acidic catalyst material and this therefore represents a problem different and independent from the problem of balancing catalyst component strengths.

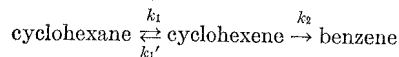
2. Hydrocracking Selectivity

When the molecular weight of high carbon number paraffins is to be lowered by hydrocracking, with a minimum of light gas production, there also are encountered two types of selectivity problems. Catalyst acidity and operating conditions are now to be chosen (see scheme XIV) to *maximize* the Y_2 reactions as leading to the desired products, which generally implies that the Y_1 reactions are still faster (see Fig. 14) and tend to push the isomer distribution toward equilibrium.

One problem is again a matter of relative component strengths in that now k_{Y_2}/k_{X_2} is to be sufficiently large. After this, the remaining product selectivity problem is a more subtle one relating to the statistics of position of the bond ruptures in the Y_2 -process which determines the heavy to light product ratios of this intrinsic process (e.g., as illustrated by Fig. 12).

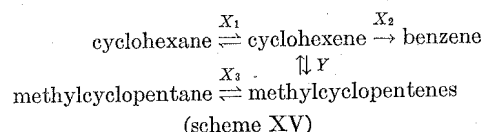
D. REACTIVITY FOR CYCLOHEXANE

The conversion of cyclohexanes to aromatics is a classical dehydrogenation reaction which will readily take place on many transition metals and metal oxides. On chromia-alumina Herington and Rideal (3) have demonstrated the occurrence of cyclo-olefin intermediate products. Weisz and Swegler (25) have demonstrated the effect on benzene yield of allowing early diffusional escape of cyclo-olefin from the porous catalyst particle. Prater *et al.* (26) have developed evidence that cyclohexene occurs as a quasi-intermediate in aromatization catalysis over platinum catalyst also, although at a smaller concentration, because of a larger ratio of effective rate constants k_2/k_1 in the scheme



for platinum catalysis compared to chromia catalysis.

Cyclo-olefins are subject to structural isomerization in contact with acidic catalysts, as Bloch and Thomas (27) and Greensfelder and Voge (21) have shown. Therefore, such catalytic activity when intimately coupled to the aromatization reaction may direct the reaction path to products having five-carbon ring structures which cannot aromatize:



The quasi-intermediate cyclo-olefin of the monofunctional dehydrogenation reaction thus becomes a true intermediate in the dual functional naphthene ring isomerization, by a process of interception, as discussed in Sections II,B,3 and II,E,1.

Conditions for this interception, leading to methylcyclopentane at the expense of benzene, must include a sufficiently large ratio of the rate constants k_Y/k_X , and favorable thermodynamic conditions. These can be realized, for example, at 450°C. under hydrogen pressure conditions such as 20 atm. of hydrogen and 5 atm. hydrocarbon partial pressure. In Table V below are shown the results from converting cyclohexane under these conditions with platinum catalyst containing the acidic component in increasing intimacy. Catalysts B, C, and D are the mechanical mixture catalysts with 1000 μ and 100 μ component particle size of the *n*-heptane isomerization study above (see Section IV,A,2). Catalysts A and E are the platinum component alone (Pt/SiO₂) and the directly impregnated dual functional catalyst from that study, respectively.

TABLE V
Diversion of Cyclohexane \rightarrow Benzene Reaction to Methylcyclopentane Formation

Catalyst	Products per 100 parts cyclohexane charged		
	Benzene	Methylcyclopentane	C-hexane (unconverted)
A Pt component alone	85	1.5	9
B 1000 μ mixture	84	6	8.5
C 100 μ mixture	57	20	7.5
D 5 μ mixture	59	23	8.5
E impregnated catalyst	40	40	7

E. AROMATIZATION OF ALKYL CYCLOPENTANES

This reaction is easily shown to follow the polystep reaction mechanism via diffusing intermediates. Actually the reaction path is already contained

in scheme XV, wherein it is desired to selectively favor isomerization over aromatization. It is interesting for several reasons (temperature and pressure effects, "trivial" to a case of a catalyst under the former conditions, sufficiently large concentrations of intermediates, phenomena related to catalytic reaction paths, can be stated).

1. Demonstration Using

Hindin *et al.* (18) published results for the conversion of methylcyclopentane to benzene on silica-alumina bearing particles and silica-alumina at 500°C. temperature. Under these conditions, the conversion of a cyclopentane to benzene is high. Consequently, the first step

Conversion of Methylcyclopentane

10 cc. SiAl
10 cc. Pt/SiO₂
SiAl + Pt/SiO₂

large conversion to "intermediate" mixture of relatively large molecules, the reaction and representation II,C). However open to the identity and behavior of the intermediate.

Table VI shows results for the conversion of methylcyclopentane (MCP) to benzene at $P_{MCP} = 0.2$ atm., with X silica-alumina, as catalyst

ization in contact with
[Greensfelder and Voge
when intimately coupled
action path to products
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benzene

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ctional dehydrogenation
ual functional naphthene
as discussed in Sections

ethylcyclopentane at the
rge ratio of the rate con-
ditions. These can be
pressure conditions such
partial pressure. In Table
cyclohexane under these
the acidic component in
the mechanical mixture
icle size of the *n*-heptane
Catalysts A and E are the
directly impregnated dual

ethylcyclopentane Formation

parts cyclohexane charged	
ethylcyclo- pentane	C-hexane (unconverted)
1.5	9
6	8.5
20	7.5
23	8.5
40	7

LOPENTANES






distep reaction mechanism
n path is already contained

in scheme XV, wherein the reactant now is the methylcyclopentane and it is desired to selectively follow the path to benzene. A study of this reaction is interesting for several reasons. By a choice of experimental conditions (temperature and pressures) one can create a transition from a case of a "trivial" to a case of a "nontrivial" polystep reaction. While operating under the former condition, one can obtain the olefinic reaction species in sufficiently large concentrations to demonstrate their identity. Also, phenomena related to catalyst selectivity, i.e., to the choice between alternate reaction paths, can be studied in this case.

1. Demonstration Using Atmospheric Pressure, Large Particle Mixtures

Hindin *et al.* (18) published data showing benzene formation to proceed readily from methylcyclopentane over mechanical mixtures of platinum bearing particles and silica-alumina, at atmospheric pressure and near 500°C. temperature. Under these conditions the equilibrium constant for conversion of a cyclopentane to a cyclopentene is of the order of unity. Consequently, the first step, if it is catalyzed by X, can itself proceed with

TABLE VI
Conversion of Methylcyclopentane over Single and over Coarse Particle Mixed Catalysts,
at Dehydrogenative Conditions

	Liquid product analysis (mole %)			
		\xrightleftharpoons{X} 	\xrightleftharpoons{X} 	
		$\Uparrow Y$ 	\xrightarrow{X}	
10 cc. SiAl	98	0	0	0.1
10 cc. Pt/SiO ₂	62	20	18	0.8
SiAl + Pt/SiO ₂	65	14	10	10

large conversion to "intermediates" at atmospheric pressure. Thus, a mixture of relatively large component particle size should indeed produce the reaction and represents a case of the "trivial" polystep reaction (Section II,C). However operating under such conditions allows us, to study the identity and behavior of analyzable quantities of intermediates.

Table VI shows results (19) of liquid product analyses from methylcyclopentane (MCP) converted under conditions of $p_{H_2} = 0.8$ atm. $p_{MCP} = 0.2$ atm., with $X = 0.3$ wt. % Pt on SiO₂ and $Y = 420$ m.²/g. silica-alumina, as catalyst components in 0.8–1.4 mm. particle size, and with

2.5 sec. residence-time. They demonstrate the production of cyclo-olefin from methylcyclopentane over platinum component alone, and the cooperative conversion to benzene when both components are present. Moreover, under these operating conditions, Pt-component is seen not only to create methylcyclopentene, but also appreciable quantities of methylcyclopentadiene. (The second column contains the sum of both mono-olefin species which were not resolved by the mass-spectrometric procedure.)

Furthermore, the principle of interception (Section II,E,1) is well illustrated if we consider the methylcyclopentane \rightarrow methylcyclopentadiene reaction as the platinum catalyzed reaction as being diverted by the Y-component, through the intermediate cyclo-olefin (here grossly detectable).

2. Nontrivial Conditions

A transition to nontrivial polystep conditions can easily be made by increasing pressure and/or lowering temperature. At 380°C., and 12 atm. pressure, equilibrium partial pressure of cyclo-olefin is of the order of 10^{-3} atm. and the equilibrium conversion for the first step is then no greater than 0.1%. The required particle intimacy (component particle size) now approaches that in the case of *n*-heptane isomerization above. Table VII below shows an experimental demonstration of the mixed component catalyst operation under these conditions.

TABLE VII
Conversion of Methylcyclopentane under
Nontrivial Polystep Conditions (Hydrogenative Condition)
($T = 380^\circ\text{C.}$, $p_{\text{H}_2} = 10.3$ atm., $P_{\text{MCP}} = 1.1$ atm., $\tau = 7.5$ sec.)

Mixed catalyst	Component particle size (μ)	Products (wt. %)	
		Benzene + cyclohexane	C ₁ - C ₆ Paraffins
Pt/Al ₂ O ₃ + Silica-alumina {	500	3.3	12.5
	5	20.0	5.6

When the required intimacy has been provided, the polystep conversion to six-carbon ring products is seen to be successfully accomplished even at this low temperature by the coaction of the separate catalyst components. In addition, we observe here again the phenomenon of *reducing* the rate of production of certain products by providing *more* intimate contact with a second catalyst component: the hydrogenolysis reaction of C—C bonds to C₁ to C₆ paraffins is inhibited; i.e., *diverted* to a new reaction path.

3. Selectivity of Alkylcy

We have thus observed phenomena:

Under *dehydrogenative* (seen in Table IV), the methylcyclopentadiene catalyst centers (Y),



to produce six-member made.

Under *hydrogenative* Pt-catalyzed reaction. I similarly explained on t



The amount of conversion of an effective component)—see Section hydrogenolysis products component which is just sufficient (II,E,2). This case is analogous described for *n*-hexane i

Using mixed catalysts microcatalytic technique above mentioned phenomenon effective catalyst acidity size of the mixture. A large (X) is then obtained for

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under
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atm., $\tau = 7.5$ sec.)

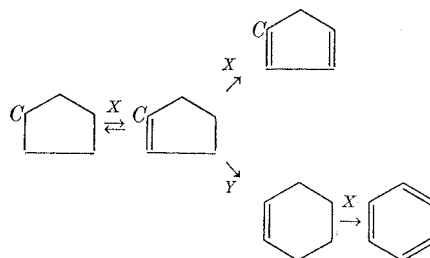
Products (wt. %)	
benzene + cyclohexane	C ₁ - C ₆ Paraffins
3.3	12.5
20.0	5.6

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essfully accomplished even
he separate catalyst come
ne phenomenon of *reducing*
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hydrogenolysis reaction of
e., *diverted* to a new reaction

3. Selectivity of Alkylcyclopentane Aromatization

We have thus observed above the following type of selectivity phenomena:

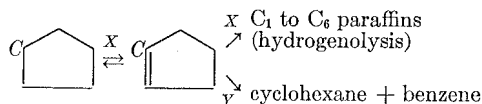
Under *dehydrogenative* conditions (510°C. and atmospheric pressure, as seen in Table IV), the double step reaction over platinum leading to methylcyclopentadiene is intercepted by the introduction of "acidic" catalyst centers (Y),



(scheme XVI)

to produce six-membered rings at the expense of the products formerly made.

Under *hydrogenative* operating conditions, hydrogenolysis is the major Pt-catalyzed reaction. Its inhibition when the Y-path is introduced can be similarly explained on the basis of the reaction scheme



(scheme XVII)

The amount of conversion to six-carbon rings should then depend on provision of an effective and high rate constant for the Y-step (acidic component)—see Section II,E,1—and the selectivity (i.e., minimizing hydrogenolysis products) should be controllable by providing an X-component which is just sufficiently large, but not excessively so (see Section II,E,2). This case is analogous to the case of minimization of hydrogenolysis described for *n*-hexane isomerization in Section IV,C,1.

Using mixed catalysts of platinum/alumina and silica-alumina, and the microcatalytic technique (both as described in Section IV,C,1) each of the above mentioned phenomena can be amply demonstrated. A wide range of effective catalyst acidity (Y) is obtained by varying component particle size of the mixture. A large spectrum for the platinum component strength (X) is then obtained for each case by starting with highly active "fresh"

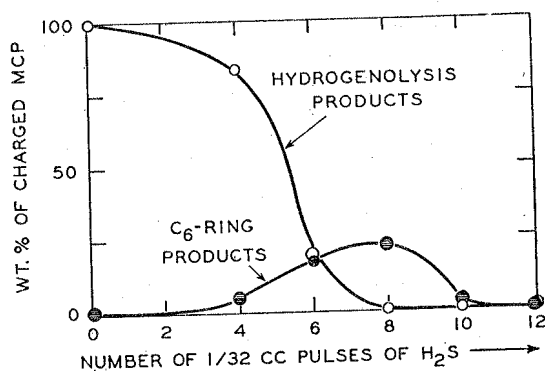


Fig. 16. Reaction of methyleyclopentane to C₆-ring hydrocarbons (benzene + cyclohexane), and to hydrogenolysis products, on dual-component mixed catalyst, when platinum component is progressively deactivated by hydrogen sulfide.

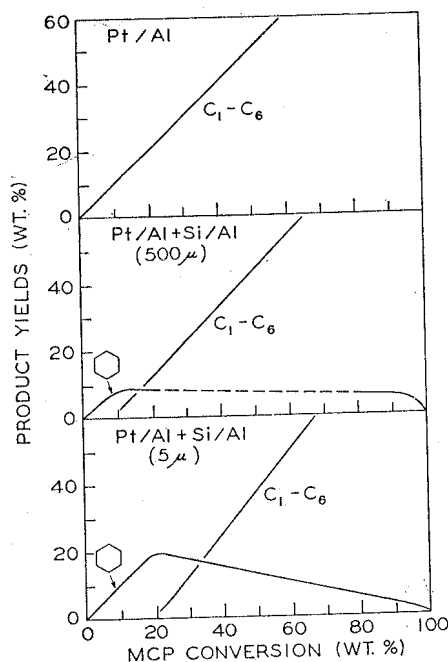


Fig. 17. Methyleyclopentane conversion to 6-membered ring products (benzene + cyclohexane) and hydrogenolysis products, for Pt-component alone, and for mixtures with silica-alumina of two degrees of intimacy, when Pt-component activity is varied.

catalyst, and progressive additions of gaseous conversion tests, at 330°C.

For the intimate (5μ) results in the results shown conditions leads to optimum deactivation control products (benzene + cyclohexane) insufficient.

The results of these studies show that the effective acidity (Y), i.e., having 500 and 5μ components used as a convenient absolute measure of the behavior of the catalyst, the analogous model of shown in Figs. 6a and b for maximum isomerization a Y-component, and is essentially appears that the acid catalytic step in the dual functional catalysts, as indicated for and Prater (28), and indication of various naphthene isomerization as shown by

V. The Petroleum

The "reforming" of petroleum at 200°C. to high octane gasolines in industrial catalytic operations (reforming) when the number of catalysts exceeds 20, the processes involved are polystep hydrocarbon conversion. A review of the art by (19).

The major objective of the reforming process is to bring the feed to equilibrium, and the product octane number is often used as a measure of conversion. Traditionally, the temperature for the reformate. Although the choice for a variable denotation of the process. In discussions of mechanisms, the octane number is a good measure of conversion concerning a large variety of feedstocks to a fixed boiling range shown

catalyst, and progressively deactivating the platinum function by successive additions of gaseous hydrogen sulfide between methylcyclopentane conversion tests, at 330°C. (other conditions as in Section IV,C,1).

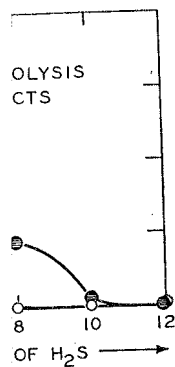
For the intimate (5μ particle) composite, such control of the X-function results in the results shown in Fig. 16. The "fresh" platinum, under these conditions leads to complete hydrogenolysis of methylcyclopentane. Platinum deactivation controls the reaction, optimizing the isomerization products (benzene + cyclohexane), until the generating step itself becomes insufficient.

The results of these studies are collected in Fig. 17 for three levels of effective acidity (Y), i.e., for the Pt-component alone, and for the mixtures having 500 and 5μ component particle size. Total conversion has been used as a convenient abscissa for comparing the three cases. Note the similarity of the behavior of the second and third cases to those calculated for the analogous model of selectivity control in Section II,D,2; this model is shown in Figs. 6a and b for two levels of activity of the Y -component. The maximum isomerization activity depends on the effectiveness of the acidic Y -component, and is essentially nil without the added Y -component. It appears that the acid catalyzed reaction step is generally the rate controlling step in the dual functional hydrocarbon reactions over platinum containing catalysts, as indicated for the naphtha "reforming" conditions by Weisz and Prater (28), and indirectly concluded from comparisons of aromatization of various naphthenes by Keulemans and Voge (29), and for paraffin isomerization as shown by Sinfelt *et al.* (30).

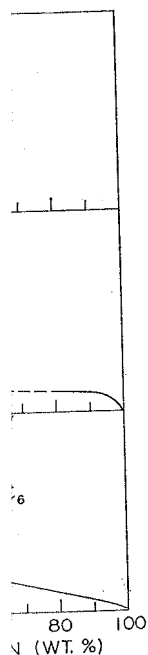
V. The Petroleum Naphtha "Reforming" Reaction

The "reforming" of petroleum fractions boiling between about 90 and 200°C. to high octane gasolines constitutes one of the largest scale industrial catalytic operations of our times. The quantity processed over platinum catalysts exceeds 2×10^8 liters/day. A majority of the reactions involved are polystep hydrocarbon conversions (see refs. 10, 11, and the extensive review of the art by Ciapetta *et al.*, 31).

The major objective of reforming is the isomerization of paraffins close to equilibrium, and the production of a maximal amount of aromatics. The octane number is often used as a measure of reforming activity or, alternatively, the temperature needed to accomplish a given octane number for the reformat. Although an octane number may not seem to be a good choice for a variable denoting catalytic activity performance in research or discussions of mechanisms, this turns out to be quite acceptable as a fairly good measure of conversion to aromatics: Fig. 18 shows a collection of data concerning a large variety of reformer gasolines, which, when standardized to a fixed boiling range show a very good correlation between octane num-



g hydrocarbons (benzene + cyclohexane) over a Pt-component mixed catalyst, when hydrogen sulfide.



tembered ring products (benzene + cyclohexane) over a Pt-component alone, and for mixtures in which Pt-component activity is varied.

ber (research octane number—R.O.N.—with 3 ml. tetraethyl lead—TEL) and total aromatics content. Since at these conventional reforming severity levels the paraffin isomerization proceeds rather closely to equilibrium throughout the range, the major variable of conversion is indeed the degree of aromatics production.

Weisz and Prater (28) have pointed out that, while on platinum reforming catalysts alkylcyclohexanes will proceed rapidly to aromatics, the conversion of alkylcyclopentanes to aromatics becomes the key dual-functional reforming reaction in the neighborhood of 98 (R.O.N. with 3 ml.

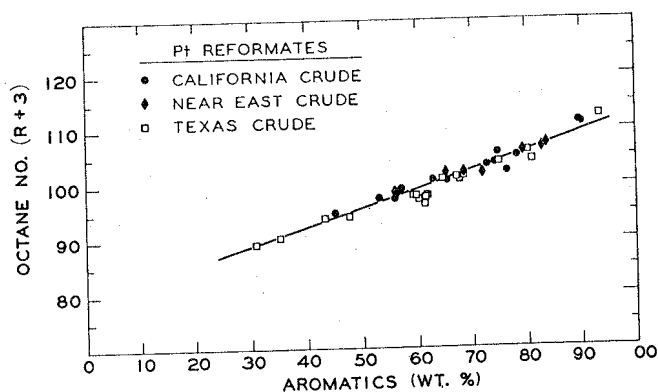


FIG. 18. Correlation between octane number and aromatics content of platinum reformed gasolines, for three different sources of naphtha.

TEL) octane number reforming severity. They have presented evidence that the catalytic strength of the acidic catalyst component is rate-controlling once the platinum component is sufficiently strong to provide the initiating step, in line with the discussions in Section IV,E. They showed the reforming temperature required to attain 98 R.O.N. to be well correlatable to the acidity measured by a cumene cracking test across a variety of acidic catalyst compositions including platinum on silica alumina, silica-magnesia, and aluminas activated by chlorine, fluorine, and boron. Figure 19 is a reproduction of the correlation originally presented; however, there are now identified compositions (marked with crosses) in which platinum component and "acidic" components were mechanically separate and were obtained by pelletizing mixtures of $\sim 5\mu$ particles platinum/silica or platinum/alumina with the acidic components. In this correlation, these reforming catalysts are seen to be indistinguishable from the conventional "impregnated" variety, the indistinguishability being consistent with the conclusion that in the reforming reactions on naphthas too, the two catalyst components can have individual and separate identity

CUMENE ACTIVITY
(MICROMOLES/SEC/CC)

FIG. 19. Relationship between 98 O.N. level and the activity of mixed composites.

and can operate satisfactorily with intermediates if sufficient

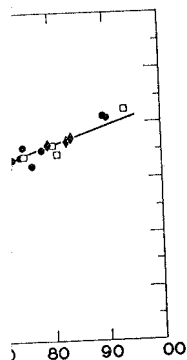
Figure 20 shows the octane number of catalysts, one of which (b) contains 0.5 wt. % platinum and

TEMPERATURE (°F) FOR 98 O.N. PRODUCT

FIG. 20. Reforming activity of impregnated and mixed-type catalyst

tetraethyl lead—TEL)
 ional reforming severity
 closely to equilibrium
 sion is indeed the degree

while on platinum re-
 l rapidly to aromatics,
 becomes the key dual-
 of 98 (R.O.N. with 3 ml.



omatics content of platinum

have presented evidence
 alyst component is rate-
 iciently strong to provide
 s in Section IV,E. They
 ttain 98 R.O.N. to be well
 ene cracking test across a
 g platinum on silica alu-
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 ation originally presented;
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 acidic components. In this
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 ridal and separate identity

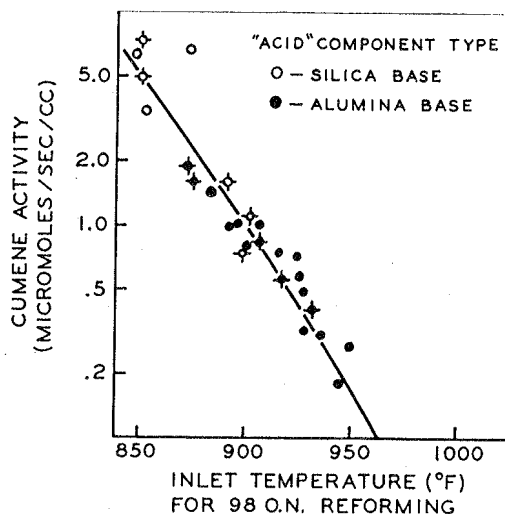


FIG. 19. Relationship between temperature requirement for reforming naphtha to 98 O.N. level and the activity of the "acidic" function. Crossed points mark mechanically mixed composites.

and can operate satisfactorily through the mediation of the gas phase intermediates if sufficient diffusional intimacy is provided (32, 33).

Figure 20 shows the operational characteristics of two reforming catalysts, one of which (b) is a conventional reforming catalyst containing 0.5 wt. % platinum and 0.5 wt. % fluorine on alumina, and the other (a)

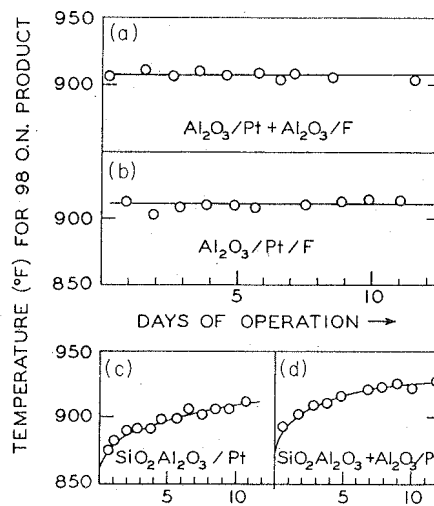


FIG. 20. Reforming activity for a twelve day period of operation, for various impregnated and mixed-type catalysts.

a 50/50 particle mixture of halogen-free alumina/1.1 wt. % platinum and alumina/0.7 wt. % F, over a period of about 12 days of operation (experimental procedures as described in ref. 28). In (c) and (d) of Fig. 20 are pictured the initial activity responses of two catalysts in which the "acidic" sites are supplied by silica-alumina of similar "over-all acidic" activity, with (c) being a silica-alumina base of 90 m.²/g. surface area impregnated directly with platinum, and (d) being a 65/35 mechanical mixture of 5 μ particles of an aged cracking catalyst of 120 m.²/g. surface area and alumina/platinum. The test conditions (apparatus) are again those described in reference 28.

The showing of adequate and equivalent operation in reforming reactions of catalysts composited from physically separate components must not be interpreted, of course, to imply that in *all* of the possible catalyst compositions, the agents or sites supplying the (de-)hydrogenation function and the "acid" function *must* be or always are independently located. For example, in the case where "acidity" and (de-)hydrogenation activity are derived from chlorine and platinum, respectively, due to the introduction of PtCl₆-ions into some aluminas by impregnation from chloroplatinic acid, it is quite likely that the two elements do not appreciably separate in the course of subsequent drying and calcination. However, it appears that, for all purposes studied, such direct proximity is not mechanistically significant. Rather, the mechanistic models that picture the catalytic components as having separate identities have provided a useful and constructive framework for further investigation and understanding of the behavior of this type of catalyst, as evidenced by the development and use of functional tests (28; 31, p. 522; 23) studies of mechanisms of catalytic deactivation, etc.

Another example for the use of the mixed catalyst concepts in mechanistic studies can be found in investigations concerning aging mechanisms. For example, experiments, such as those pictured in Fig. 20, using various mixed composition, supply pertinent information. In reforming operations under conditions described above, the initial fast-to-slow deactivation transition [(c) in Fig. 20] is characteristic of platinum on silica base impregnated catalysts, while "flat" or gradually rising temperature requirements are encountered with good alumina-type reforming catalysts. The observation that the fast-to-slow response occurs also with the silica-alumina + alumina/Pt mixed catalyst [(d) in Fig. 20] suggests that this particular initial deactivation response is characteristic of the type of acidic site and not of the platinum support as such. In further confirmation of this, Weisz, Prater, and Swegler (unpublished) have tested mixed compositions using alumina/F as acidic component with platinum on silica and were able to

obtain "flat" activity regardless of the initial aging procedure. (Weisz and Prater (28), and (34).)

One reaction occurring discussed in this review is the contribution to the reforming conditions so far discussed. The content of this reaction is additional aromatics. However, the offer a clear picture of the reforming catalyst functions. The correlation between cyclization and the amount of hydrogenation is a superior activity. They suggest a "critical spacing"; beyond which would not appear catalyst that the extractable form perhaps due to their great to whether or not these (de-)hydrogenative function to interpret dehydrocyclization beyond the elementary (cyclohexanes under usually inadequate for the very high specific rate conditions and mass diffusion effects. for this (see ref. 28; and 3

VI. C

A. THE XYLENES

The isomerization reaction of the acidic catalysts, such as ethyl-benzene will not proceed *if* a reaction *will* proceed *if* a furthermore, such conversion, i.e., by conditions favoring that the xylenes to ethylbenzene in a polystep fashion according

1 wt. % platinum and
rs of operation (experi-
and (d) of Fig. 20 are
s in which the "acidic"
er-all acidic" activity,
rface area impregnated
chanical mixture of 5 μ
surface area and alu-
e again those described

n in reforming reactions
omponents must not be
ssible catalyst composi-
rogenation function and
pendently located. For
rogenation activity are
due to the introduction
ion from chloroplatinic
ot appreciably separate
m. However, it appears
y is not mechanistically
cture the catalytic com-
d a useful and construc-
standing of the behavior
opment and use of func-
ms of catalytic deactiva-

t concepts in mechanistic
aging mechanisms. For
Fig. 20, using various
In reforming operations
ast-to-slow deactivation
um on silica base impreg-
emperature requirements
g catalysts. The observa-
ith the silica-alumina +
gests that this particular
ne type of acidic site and
nfirmation of this, Weisz,
nixed compositions using
n silica and were able to

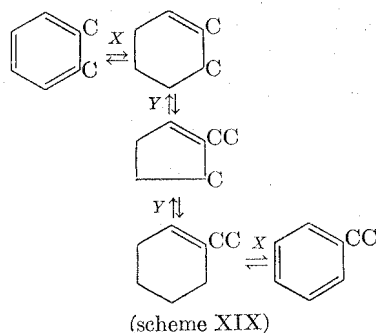
obtain "flat" activity responses. Evidence for the role of acidic sites in at least the initial aging processes of reforming catalysts was presented by Weisz and Prater (28), and probable mechanisms discussed by Myers *et al.* (34).

One reaction occurring in the reforming process and which has not been discussed in this review is the cyclization-aromatization of paraffins. Its contribution to the reforming reactions is a secondary one at the severity conditions so far discussed. When processing to increasingly higher aromatics content this reaction gains increasing importance as a source for additional aromatics. However, the published literature does not as yet offer a clear picture of reaction paths and the specific contributions of the catalyst functions. McHenry and co-workers (35) present data showing a correlation between cyclization-aromatization activity of platinum catalysts and the amount of Pt extractable with HF or acetylacetone, and suggest that platinum in a special complex with the alumina surface has superior activity. They suggest a combination of platinum with an acidic site at a "critical spacing"; beyond the point of speculation, however, the observations would not appear capable of more specific interpretation than to show that the extractable form of platinum in their samples is more active; perhaps due to their greater degree of dispersion. A conclusive showing as to whether or not these catalysts have superior activity for their basic (de-)hydrogenative function would be desirable before attempts are made to interpret dehydrocyclization results in terms of special properties beyond the elementary (de-)hydrogenation and "acidic" functions. Tests with cyclohexanes under more or less standard operating conditions are usually inadequate for this because of the difficulties introduced by the very high specific rate constants involved and the resulting major thermal and mass diffusion effects. Very careful and special techniques are required for this (see ref. 28; and 31, p. 522).

VI. Other Polystep Reactions

A. THE XYLENES-ETHYLBENZENE INTERCONVERSION

The isomerization reactions among the three xylenes are catalyzed by the acidic catalysts, such as silica-alumina. However, the skeletal transition to ethylbenzene will not occur (36). Pitts *et al.* (37) have shown that such reaction *will* proceed if a (de-)hydrogenation component is also present; furthermore, such conversion is favored by lowering of operating temperature, i.e., by conditions favoring hydrogenation. One is led to the conclusion that the xylenes to ethylbenzene "skeletal" rearrangement takes place in a polystep fashion according to



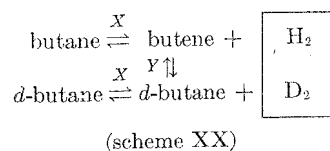
that is, by ring contraction and expansion steps of cyclo-olefin intermediates catalyzed by the acidic component (38) and analogous to those occurring in the hydroisomerization reactions of cyclohexanes and alkylcyclopentanes described earlier above.

P. S. Nix and S. Lucki, at our laboratories, have demonstrated (unpublished) the ability of *separate* platinum and acidic catalysts, as a mixed composite, to perform the skeletal transition from ethylbenzene to xylenes under hydrogenative conditions ($p_{H_2} = 11.8$ atm., $p_{EB} = 1.2$ atm.; 427°C , $\tau = 3.3$ sec.) with 40% conversion to xylenes. Yet at the same temperature, but at atmospheric pressure where production of cyclo-olefin intermediates is not favored, they obtained no measurable conversion even with platinum directly impregnated on the silica-alumina.

B. HYDROGEN EXCHANGE BETWEEN PARAFFIN HYDROCARBONS

Myers *et al.* (39) have studied the deuterium exchange between two paraffins, i.e., between deuterobutane and butane, on a variety of dual-functional catalysts (various impregnated types of platinum-acidic oxides). They find that the hydrogen exchange correlated primarily with the (de-)hydrogenation activity of the catalyst, but in addition, an appreciable positive correlation with "acidic" activity was demonstrated, which led the authors to conclude that this "may mean that acid sites and platinum sites coact to promote the latter effect."

It is reasonable to suspect that a dual functional reaction path exists following the scheme,



such that direct exchange interaction among olefin intermediates reacting on acidic sites (Y) add to the net rate of exchange. The existence of such

vapor phase transfer mechanism the mixed catalyst technique

C. ORGAN

Rylander and Cohn (40) have used catalysts simultaneously of metals in the reduction of Fig. 21 are plotted observa

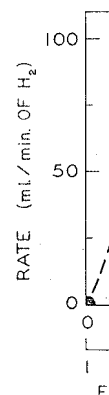
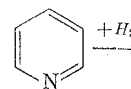


FIG. 21. Rate of butyne-1,4-diol Pd and Ru catalyst (after Rylander).

butyne-1,4-diol using 300 mg of methanol solvent at ambient of palladium or ruthenium proportions. The total weight of in all cases.

Similar effects were demonstrated in the reduction of pyridine, nitriles and of nitrobenzene as large synergistic effects with carbon particles, one may be property of some chemical elements. As the authors point out differing catalytic effectiveness groups. Thus, when reductive step, such as in the case



vapor phase transfer mechanism between sites may be subject to test by the mixed catalyst technique.

C. ORGANIC REDUCTION REACTIONS

Rylander and Cohn (40) have reported synergistic effects for the use as catalysts simultaneously of *two* different platinum or palladium group metals in the reduction of various organic compounds. For example, in Fig. 21 are plotted observations concerning the rate of hydrogenation of

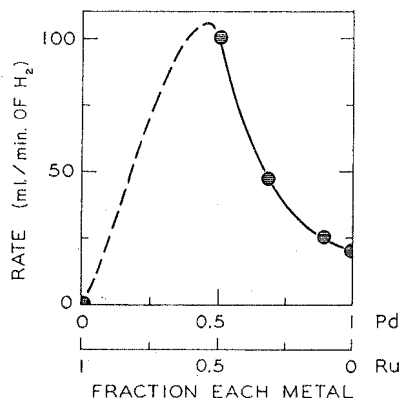
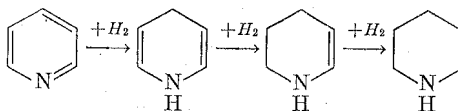


FIG. 21. Rate of butyne-1,4-diol reduction vs. relative composition of a composite Pd and Ru catalyst (after Rylander and Cohn, 40).

butyne-1,4-diol using 300 mg. of catalyst, 200 mg. of reactant, and 100 ml. of methanol solvent at ambient conditions, wherein the catalyst consisted of palladium or ruthenium or both, precipitated on carbon in varying proportions. The total weight of the precious metal was 5 wt. % of the catalyst in all cases.

Similar effects were demonstrated by them for palladium and ruthenium in the reduction of pyridine, and for ruthenium and platinum in the reduction of nitriles and of nitrobenzenes. Since they show similar although not as large synergistic effects when the two metals are introduced on separate carbon particles, one may be sure that the enhancement is not an intrinsic property of some chemical combination or contact between the different metals. As the authors point out, the various metals are known to have differing catalytic effectiveness for the reduction of different functional groups. Thus, when reduction takes place via more than one chemical step, such as in the case



cyclo-olefin intermediates analogous to those occurring in the reduction of cyclopentadiene and alkylcyclopentanes

as demonstrated (unpublished) for the reduction of ethylbenzene to xylenes at $p_{EB} = 1.2$ atm.; 427°C . At the same temperature, cyclo-olefin intermediates are formed even with platinum

HYDROCARBONS

exchange between two metals, on a variety of dual-metal catalysts (e.g., platinum-acidic oxides). It is noted primarily with the addition, an appreciable enhancement is demonstrated, which led to the conclusion that acid sites and platinum

an alternative reaction path exists

in intermediates reacting with hydrogen. The existence of such

one may expect specific effects from combinations of metals each of which contribute different rate constants to various of the steps. In some cases the intermediates may be well identifiable in analyzable quantities; in other cases they may occur at subdetectable concentrations. It would appear that the mixed catalyst techniques together with quantitative appraisals based on principles outlined above may give more information on the concentration and nature of the intermediates in various cases. By way of illustration, the reaction rates reported in this work were of the order of $dN/dt = 10^{-4}$ moles/sec./cc. catalyst. With a liquid phase diffusivity of intermediates of molecular weight similar to that of reactant estimated at $D = 5 \times 10^{-6}$ cm.²/sec. we have from (15) (see also Section IV,A,1)

$$20R^2/[B] \sim \Phi$$

From the relative rates observed for separate particles and of coprecipitated metal (assumed to offer complete intimacy for the intermediate) we might estimate Φ (see ref. 6) as of the order of magnitude $\Phi \sim 3$ in Rylander and Cohn's observation, which leads for various catalyst particle sizes (carbon granules) to an estimate of concentration of intermediate as follows:

R	=	10	100	1000	μ
$[B]$	\approx	7×10^{-6}	7×10^{-4}	7×10^{-2}	moles/cm. ³
$B\%$	\approx	0.2	20	—	% in liquid

These figures suggest that in this case intermediates occurred at potentially analyzable quantities.

It seems clear from the interesting observations of Rylander and Cohn (40) that the catalytic possibilities using polyfunctional catalyst should increase rapidly in number when one deals with increasingly complex organic structures, where many more individual reaction steps become possible.

D. UNSUSPECTED QUASI-INTERMEDIATES AND POLYSTEP REACTIONS

Certain catalyst materials that may not have been considered to operate as multifunctional catalyst composites may in fact be operative via distinct and separate catalytic sites. Keulemans and Schuit (41) have discussed such possibilities briefly. In this article, we shall not look further into these possibilities; however, inasmuch as we have examined various reactions and reaction sequences, it is very appropriate to point out that there undoubtedly exist reactions which have been considered to be catalyzed essentially by monofunctional systems, but which may in fact undergo polystep conversion. Also, quasi-intermediates may exist, appearing as traces of side products or remaining undetectable, that carry a ready

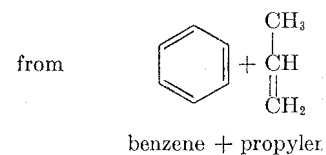
potential to be "operated" in a manner described in Section IV.

Example: Cumene Cracking

An example for this phenomenon is given by Weisz and Prater (28), pictured simply as



When this reaction rate was found not to be controlled by the rate of diffusion in a Schwab type differentiator, this rate was found not to be controlled by the rate of diffusion of the component into the catalyst, but remained controlled by the rate of reaction produced, and of the liquid phase.

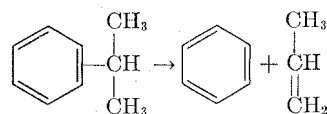


Examination of this phenomenon led to the demonstration of the same effect in an integral reactor, at 400°C and 1 atm. and constitution of the gas phase. (a) with 420 m.²/g. silica-alumina, (b) with a pelleted 5μ size silica-alumina, (c) with a pelleted 5μ size silica-alumina, (d) with a mixture of silica-alumina and alumina. Under severe conditions of high pressure and temperature, when the two-component mixture is made, the shift of the equilibrium in the presence of whole pellets is not observed (d), but approximately the same. Weisz carried out a study and found a maximum transition time near 10–30μ. This corresponds to a rate of about 10⁻⁵ atm. by II,D,3 and III. This would indicate that the quasi-intermediate from the intermediate may well be

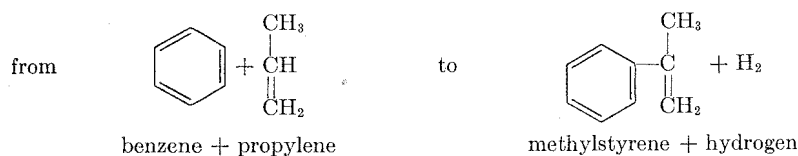
potential to be "operated upon" by a second catalyst component, in the manner described in Section II,E,3.

Example: Cumene Cracking

An example for this phenomenon appears to exist in observations reported by Weisz and Prater (28) on cumene cracking. This reaction is usually pictured simply as



When this reaction rate was measured by the rate of molar gas formation in a Schwab type differential reactor (28, 28a) over silica-alumina catalyst, this rate was found not greatly affected by the introduction of a platinum component into the catalyst mass; the observed gas formation rate remained controlled by the acidic activity alone. Yet, an analysis of the gas produced, and of the liquid product, showed a shift in product composition



Examination of this phenomenon was continued by J. Wei, who was able to demonstrate the same effect under gross conversion conditions, that is, in an integral reactor, at 478°C. Figure 22 shows the results for the extent and constitution of the gaseous product for four cases: (a) with pellets of 420 m.²/g. silica-alumina, (b) with pellets of 0.6 wt. % platinum on alumina, (c) with a pelleted 5μ size particle mixture of the two components (a) and (b), and (d) with a mixture of pellets of each component. Even under these severe conditions of high conversion (60–90%) where some by product gases are made, the shift of gas composition is amply demonstrated when the two-component mixture is in good mutual intimacy (c). The mere presence of whole pellets of both types of catalysts does not show this effect (d), but approximates simple additivity of products from each component. Wei carried out a study with varying component particle size, and found a maximum transition to hydrogen production to occur somewhere near 10–30μ. This corresponded to a vapor pressure of the quasi-intermediate of about 10⁻⁵ atm. by application of the principles outlined in Sections II,D,3 and III. This would correspond to a free energy of formation of the quasi-intermediate from cumene of about +16 kcal/mol. The quasi-intermediate may well be represented as a very low level side product of

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POLYSTEP REACTIONS

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various participating enzymes of a reaction sequence are *not* uniformly and homogeneously dispersed, we have a situation rather analogous to that of the mixed or polyfunctional heterogeneous catalyst systems described in this chapter. We should be able to apply intimacy criteria as in Section II,D to estimate the maximum distance which may exist between enzyme systems involved in the same polystep reaction sequence. If we make the assumption that such enzyme systems must be contained within the biological cell, then such an estimate will define the maximum allowable cell dimension, in the absence of hydrodynamic means for mass transport within it.

1. Cell Dimensions

In Section II,D,1 we have developed an expression, formula (7), for the maximum dimension between two parallel planes representing the two different catalytic surfaces of a reaction sequence, containing the reaction rate *per unit surface area*. Now let us imagine a reaction space (of unit volume) filled with such surfaces of catalyst X and Y. Then, the number of such planar reaction units will be $n = 1/L$, and the maximum attainable reaction rate *per unit volume* will be

$$\left(\frac{dN_v}{dt}\right)_{\max} = [B_{\text{eq}}] \frac{D}{L^2}$$

or, for a given magnitude of reaction rate to be achieved, the maximum allowable dimension for separation of catalyst types is given by

$$L \leq \left(\frac{D[B_{\text{eq}}]}{dN/dt}\right)^{1/2} \quad (20)$$

The form of this criterion is identical to that of formula (15) for porous catalyst components. However, there it defines conditions for the onset of reaction inhibition, while here it sets an absolute ceiling.

For a biochemical process by enzyme systems located at some distance from each other, we might now estimate the maximum dimension L from the magnitudes of the reaction-rate to be accomplished dN/dt , and the concentration of the intermediate species B_{eq} involved.* We may expect the diffusivity to be of a magnitude typical for large molecular species in an aqueous medium, i.e., $D \approx 10^{-6}$ cm.²/sec.

The metabolic rate of oxygen uptake by various organs, cells, and bacteria is of magnitude 10^{-2} cc. O₂/min./g., or $dN/dt \sim 10^{-8}$ moles/sec. cm.³. Let us take this as a typical rate magnitude. (Presumably there are many

* We will assume that the actual concentration does approach the attainable equilibrium concentration, i.e., that the enzyme catalyst has developed to fairly optimum activity.

specific reaction processes going on at a smaller rate than the over-all respiratory process, which, however, would also be confined to more specific and thus smaller volumina of the body.)

We thus find the following dimensions L for various concentrations of reaction intermediates:

$[B] \frac{\text{moles}}{\text{cm}^3}$:	10^{-12}	10^{-10}	10^{-8}	10^{-6}	10^{-4}	10^{-2}
$L, \text{cm.}$:	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1

Now what are typical magnitudes for concentration of intermediate reacting species in oxygen metabolism? Cell respiration is seriously inhibited by 0.5×10^{-8} moles/cc. of a poisonous ion, such as cyanide, indicating that some important species must exist at a concentration as low as this (see e.g., ref. 42). The concentration of cytochrome c in yeast cells is found to be of magnitude 10^{-8} moles/cc. With such concentration magnitudes indicated, and assuming that the concentration of an enzyme specific for a given reaction will not greatly exceed in magnitude the concentration of the species to be reacted, we obtain for the maximum allowable dimension

$$L \sim 10^{-3} \text{ cm.}$$

which is of the order of actual cell dimensions, i.e., about 5×10^{-4} to 5×10^{-3} cm.

It is interesting to note that the criterion, formula (20), contains the quotient $(dN/dt)(1/[B_{eq}])$ and to observe that there appear many situations where for a given type of process this ratio of chemical rate to intermediate

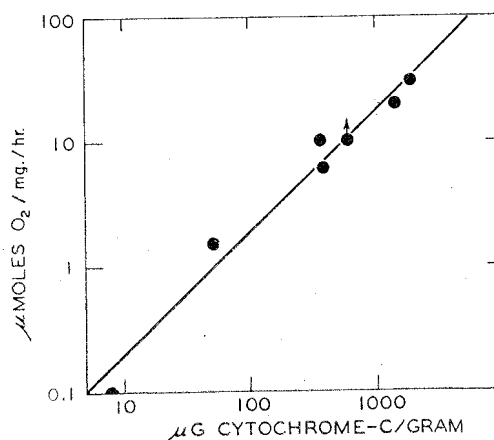


FIG. 23. Respiration rate and cytochrome c concentration in various types of rat tissue (after Pappenheimer and Hendee, 43).

concentration indeed tend each of these quantities in as, for example, in the m on respiration rate and cy which data Fig. 23 is draw

These observations mig of the dimension of the bi an intermediate between sistent with the trend of f of specific enzymes is loca sarcosomes, etc.; see, e.g., only *one* intermediate reac transport, and our criteria

2. Turnover Numbers

It is difficult to find ma tion concerning the conce $(dN/dt)(1/[B_{eq}])$ can be tr to the biochemist (molecu of enzyme), by

$$T = \frac{e}{n}$$

From this and (20) follo

for the maximal distance

If we now use $D \sim 10^{-6}$ have

For enzyme reactions ch (the latter magnitude in r

The maximal value is : the suggestion that some turnover numbers requir dimensions.

smaller rate than the over-all
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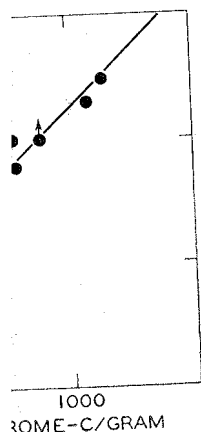
10^{-6} 10^{-4} 10^{-2}

10^{-2} 10^{-1} 1

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of chemical rate to intermediate



centration in various types of rat tissue

concentration indeed tends to be constant for various tissue even though each of these quantities may vary over nearly three orders of magnitude, as, for example, in the measurements of Pappenheimer and Hendee (43) on respiration rate and cytochrome *c* content of various rat tissues from which data Fig. 23 is drawn.

These observations might thus suggest that, generally, a good fraction of the dimension of the biological cell is involved in diffusive transport of an intermediate between two different enzyme regions. This fact is consistent with the trend of findings in cytology indicating that the activity of specific enzymes is localized within small area of the cell (mitochondria, sarcosomes, etc.; see, e.g., ref. 44). We should note that it is sufficient for only *one* intermediate reaction step of a long sequence to be subject to such transport, and our criteria will apply to the over-all reaction.

2. Turnover Numbers

It is difficult to find many specific instances with quantitative information concerning the concentration of intermediates. However, the quotient $(dN/dt)(1/[B_{eq}])$ can be transformed to the "turnover number" T familiar to the biochemist (molecules of reactant reacted per minute per molecule of enzyme), by

$$T = \frac{60}{n} \frac{dN}{dt} \frac{1}{[B_{eq}]}$$

$$n = \frac{\text{molar enzyme concentration}}{\text{molar reactant concentration}}$$

From this and (20) follows

$$L \leq \left(60 \frac{D}{nT} \right)^{1/2}$$

for the maximal distance magnitudes.

If we now use $D \sim 10^{-6}$ cm.²/sec., and n of order of magnitude unity, we have

$$L \leq 8 \times 10^{-3} / \sqrt{T}$$

For enzyme reactions characterized by turnover numbers of 10^2 to 10^6 (the latter magnitude in more exceptional cases), we obtain

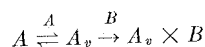
$$L \leq 10^{-3} \dots 10^{-5} \text{ cm.}$$

The maximal value is again typical of actual cellular dimensions, with the suggestion that some processes, namely, those having the very high turnover numbers require greater proximity, but *within* cellular space dimensions.

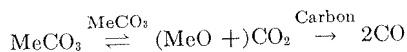
F. INORGANIC REACTIONS

There is little reason to believe that the phenomena of stepwise reaction processes and the criteria developed for them above would not be found to be operative and applicable in some circumstances of inorganic chemistry, notably in solid-solid reactions and solid-gas reactions accelerated by a second solid.

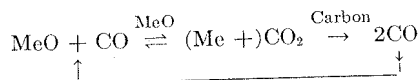
In a reaction between solids *A* and *B* in a mixture of these solids, a vapor-product *A_v* of *A* may be the agency which contacts *B*, at *B* so that the reactivity is based on



with the letters above the rate arrows again indicating the location of each process in complete analogy to scheme VIII. *A_v* may be due to a small vapor pressure of *A* itself or due to a decomposition pressure, which then would define the concentration of the intermediate [*A_v*], in applying criteria such as (15) or (20). Interesting examples and variants in detail (but not variants in principle) are such reactions as the carbonate transformation "catalyzed" by the admixture of carbon.



or the metal oxide reduction with carbon, involving the cycling of gas phase intermediate (carbon monoxide)



Many situations are encountered in solid-solid reactions where the concept of the limited point contacts being the sole surfaces of chemical interaction is a difficult one to accept. On the other hand, the numerical magnitudes which the above criteria indicate for the reaction rates at even minute intermediate vapor pressures lend credence to the possibility that these phenomena may provide the "coupling mechanism," in such cases.

VII. Conclusions

Reactions on solid catalysts can proceed by way of several distinct steps of chemical transformation, each catalyzed by distinctly different types of catalytic sites. The chemical intermediates can exist as true desorbed species in the phase above the catalyst. The kinetic steps of the sequence of reactions are coupled to each other through the processes of diffusion of these intermediates. The classical laws of diffusion create a qualitative and quan-

titative link between the steps. The criteria and principles only in catalytic hydrocarbon organic reactions, in some chemical laboratory experience,

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IONS

phenomena of stepwise reaction above would not be found to analogies of inorganic chemistry, as reactions accelerated by a

mixture of these solids, a vapor-contacts B , at B so that the

indicating the location of each, may be due to a small vapor pressure, which then would $[A_v]$, in applying criteria such as in detail (but not variants) to the transformation "catalyzed"

Carbon
→ 2CO

solving the cycling of gas phase.

Carbon
→ 2CO
↑

solid reactions where the conclusion on the other hand, the numerical magnitude of the reaction rates at even evidence to the possibility that "mechanism," in such cases.

15

any way of several distinct steps by distinctly different types of species do not exist as true desorbed species in the steps of the sequence of reaction processes of diffusion of these species to create a qualitative and quan-

titative link between the rate process and the thermodynamics of reaction steps. The criteria and principles involved have general applicability not only in catalytic hydrocarbon transformations, but also in other catalyzed organic reactions, in some of the largest scale industrial processes, in chemical laboratory experience, and in the biochemical world of life processes.

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